X-RAY INVESTIGATION OF STRUCTURAL RELATIONSHIPS AND PHYSICAL PROPERTIES IN CHARGE-TRANSFER COMPLEXES.

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by
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1980

ABSTRACT

The crystal structures of four charge-transfer complexes and two organo-metallic compounds have been determined. The various geometries encountered are related to structural isomerism and to physical properties. The charge-transfer complexes phenanthrene pyromellitic acid dianhydride (PMDA), fluorene PMDA, thianthrene PMDA and biphenyl trinitrofluorenone have planar molecules except for thianthrene which is bent. The molecule N-(2-hydroxyphenyl)salicylaldimine dimethyl tin(IV) is bipyramidal whilst the hexa-μ-dithiocacodylato tetrazinc-sulphide isomers have a tetrahedral character.

The concept of the crystalline state as a hierarchical system is developed. The physical basis, and electrical properties of charge-transfer complexes are reviewed, and the implications of structural features, and possible uses of these compounds in modern signal processing technology is discussed.

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LIST OF ABBREVIATIONS

A number of abbreviations are used throughout the text of this thesis. Their full meaning is generally indicated in the text, and most of them are also listed here.

A	acceptor
As	arsenic
C	carbon
Cl	chlorine
CNDO	complete neglect of differential overlap
CT	charge-transfer
Cu	copper
D	donor
DBC	diffracted beam collimator
DNA	deoxyribose nucleic acid
esd	estimated standard deviation
ESR	electron spin resonance
F	structure factor
H	Hamiltonian
H	hydrogen
HCNB	hexacyanobenzene
Hfs	hyper-fine splitting
I	intensity
m_e	mass of electron
Mo	molybdenum
N	nitrogen
NIPC	Naphthalene-Isopropylcarbazole picryl chloride
O	oxygen
ρ	electron density
p	linear momentum
PCNT	pentacyanotoluene
PMDA	pyromellitic acid dianhydride
RNA	ribose nucleic acid
s	angular momentum
S	sulphur

S	overlap integral
SCF	self consistent field
Sn	tin
TCNB	tetracyanobenzene
TCNQ	tetracyanoquinodimethane
TNB	trinitrobenzene
TNF	trinitrofluorenone
ZFS	zero field splitting
Zn	zinc
Zr	zirconium

MOLECULAR STRUCTURES CITED

A number of molecules are referred to in the body of this thesis. Most of their structures are detailed here, in an alphabetical sequence, for the convenience of the reader.

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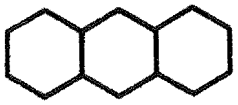

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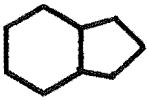

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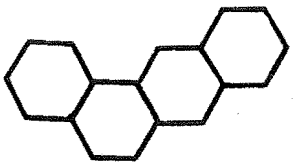

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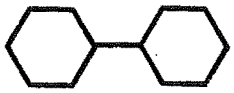

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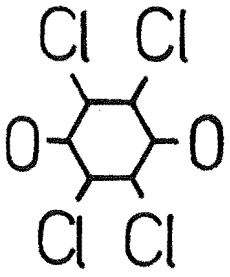

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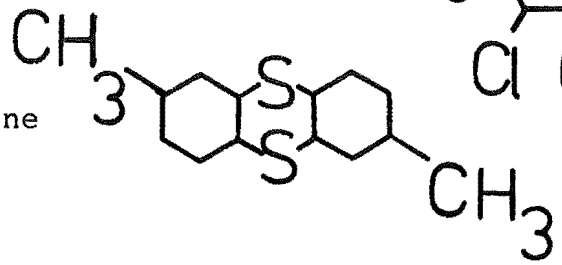

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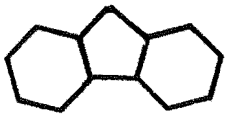

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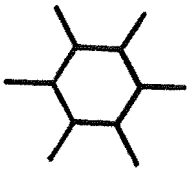

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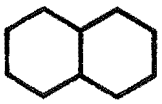

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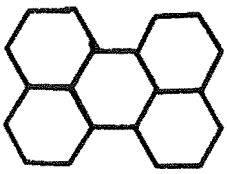

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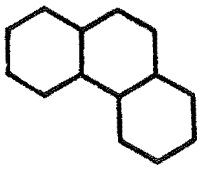

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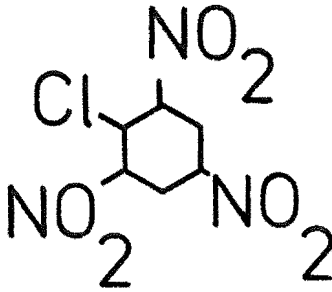

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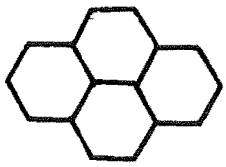

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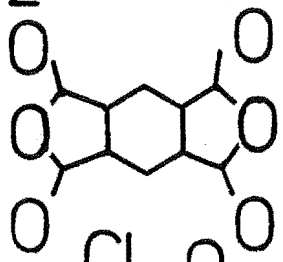

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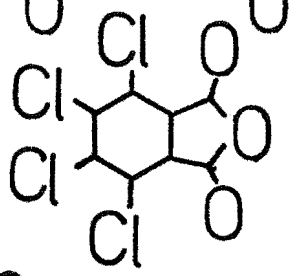

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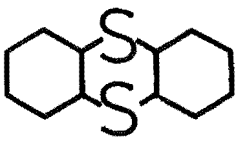

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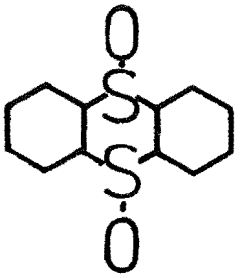
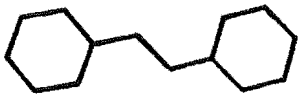
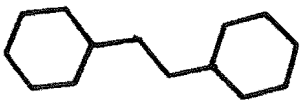
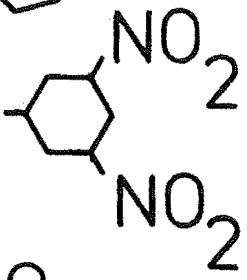
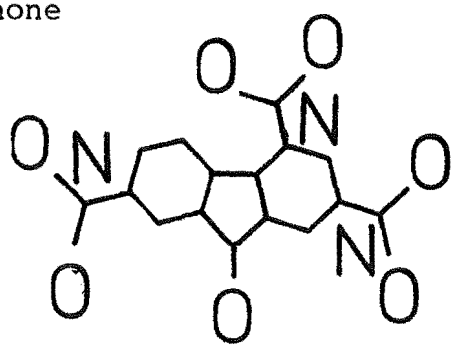


trans-4-methylstilbene 

trans-stilbene 

trinitrobenzene 

trinitrofluorenone 

UNITS USED

A number of the units used or quoted in this thesis are not according to the current standard SI convention but they do remain in common usage. Accordingly they are listed here with their standard equivalents.

$\mathring{A}$	nm	$\times 10^{-1}$
cm	m	$\times 10^{-2}$
cm^{-1}	m	$\times 10^{2}$
mm	m	$\times 10^{-3}$
Gauss	wm^{-2}	$\times 10^{-4}$

CHAPTER 1

INTRODUCTION

1.1 CRYSTALLOGRAPHIC STUDIES

This thesis covers a range of crystallographic studies using a variety of techniques. The structures of four π-π charge-transfer (CT) complexes and two organo-metallic compounds are determined. They are phenanthrene pyromellitic acid dianhydride (PMDA), fluorene PMDA, thianthrene PMDA, biphenyl trinitro-fluorenone, and N-(2-hydroxyphenyl) salicylaldimine dimethyl tin(IV) and hexa-μ-dithiocacodylato tetrazincsulphide.

Interesting disorder, isomerism and bonding features are encountered. CT compounds have interesting electrical properties discussed, but not investigated in this thesis. Models of, and features of the observed electrical behaviour in this class of compound are discussed in Chapter 2.

1.2 BASE DATA

The crystallographic studies provide very important base data, as knowledge of the arrangement of the molecules within the crystallographic unit cell is essential to a good understanding of physical properties. Knowing space group symmetry enables the correct use of selection rules for calculating energy changes in transitions between various states. Furthermore, the establishment of atomic parameters makes possible the calculation of molecular orbitals in, what must be, the minimised potential energy state. Such calculations are not part of this thesis, but the types of calculation which are made, are discussed.

1.3 THE CRYSTALLINE STATE

The concept of a crystal as a hierarchical type of structure, having various types of states, disorder, and transitions is developed. It facilitates discussion of a crystal's physical properties in terms of the molecular structures of which it may be comprised.

1.4 THE PROPERTIES OF CRYSTALLINE MATERIALS

A crystal consists of an array of identical chemical units. The internal character of an ideal crystal can be described in terms of a lattice, the smallest repeating unit of such a lattice being termed a unit cell. The unit cell described by parameters a, b, c, α, β, γ contains a number of identical chemical units related to each other by symmetry operations and to those in other cells by translations. For purposes of notation let such a cell be R, and a distinct site within a chemical unit be a, then R_a denotes the site a in the cell R. The chemical units may be single atoms, parts of molecules, molecules or sets of chemically identical (yet independent) or in some cases different molecules. The coordinates of atoms x,y,z within the unit cell are expressed in terms of fractions of the unit cell dimensions. Bounding faces and other planes in the crystal are described in terms of Miller indices hkl and are represented by points in reciprocal space. A real crystal approximates the ideal crystal described, deviating from it either by cell or lattice imperfection.

The main bulk physical properties measurable are dimensions, density, bulk modulus, shear strength, thermal conductivity, velocity of sound and refractive index. These can generally be measured without significant interaction with the interior (contents) of the crystalline material.

The electrical properties involve charge carriers within the crystal, namely electrons and holes, whose behaviour is determined by the internal character of the crystal and interactions of external origin. The degree of interaction may be considerable in the measurement of electrical and spectral properties. External influences affecting charge carrier motion are temperature, compression, electric, magnetic and strain fields and electromagnetic radiation. A hole is defined as follows. In an array of neutral atoms the ionisation of an atom by excitation of an electron leaves it positively charged. The vacant orbital into which another electron could move is called a hole and may,

as an electron shifts from an adjacent atom or crystal orbital into it, behave as a positive charge carrier. If an electron and a hole move as a pair from atom to atom or molecule to molecule they are described as an exciton.

1.5 CHARGE-TRANSFER COMPLEXES

The stochiometrically 1-1, $\pi-\pi$ charge-transfer compounds are a class of compounds currently subject to intensive study. Such physical properties as exciton motion (Mohwald & Sackmann 1974), photoconductivity (Haarer & Mohwald 1975), electron mobility (Bergman & Jortner 1974; Mohwald, Haarer & Castro 1975) and fluorescence (Kepler, Caris, Avakien & Abramson 1963) are being investigated. Techniques in use include electron spin resonance (ESR) (Dalal, Haarer, Bargon & Mohwald 1975), emission and absorption spectroscopy (Haarer & Karl 1973) and conductivity measurements (Batt, Braun & Hornig 1968). A review of crystallographic work has been made by Herbstein (1971). The commonly occurring features he discusses are (1) the donor-acceptor distance of ~ 3.5 Å, (2) stacking of the donor and acceptor molecules in semi-infinite columns, (3) disorder, (4) centrosymmetric molecules, (5) the dihedral angle between the adjacent molecules and (6) the non-perpendicularity of the planes of the component molecules with respect to the stack axis.

1.6 PYROMELLITIC ACID DIANHYDRIDE

Interest in PMDA as an electron acceptor, has led to the study of $\pi-\pi$ organic charge transfer compounds involving it and various donor molecules. These include anthracene and perylene (Boeyens & Herbstein 1965), napthalene (Herbstein 1971), pyrene (Herbstein & Snyman 1969), benzanthracene (Foster, Scrimgeour, Iball & Williams 1975), trans-stilbene (Kodama & Kumakura 1974a), trans-4-methylstilbene (Kodama & Kumakura 1974b), phenanthrene, fluorene and thianthrene (Evans & Robinson 1977, 1980a and 1980b).

1.7 ORGANO-METALLIC COMPOUNDS

N-(2-hydroxyphenyl) salicylaldimine dimethyl tin(IV) and hexa-μ-dithiocacodylato tetrazincsulphide were studied, to further work by Professor B.R. Penfold and Dr. Ward T. Robinson, respectively. The tin compound determination provided an introduction to X-ray crystallography, and the arsenic compound was the final structure determined and provided a suitably challenging finale.

1.8 COMPUTING DEVELOPMENT

The principal program developed was a shaded density line-printer plotting routine (ARTSTC), for illustrating electron density maps. A second major effort was a Patterson map investigating program (PATINV) combining a number of features which others have undoubtedly developed. A third, medium sized program, (SORTLIST) to sort structure factors, present them in publication format, and to give statistical analyses of them is presented. Two small programs SCALE and BONDSTAT written to meet certain contingencies are also given.

CHAPTER 2

FEATURES OF ELECTRON BEHAVIOUR IN CRYSTALS

2.1 INTRODUCTION

2.1.1 ELECTRON BEHAVIOUR

This section constitutes an overview of the behaviour of electrons. A free electron mass m_e, charge e has angular momentum $\underline{s}$ and linear momentum $\underline{p}$ ($|\underline{p}|>0$) and its state may be described by a wavefunction from which its energy may be deduced using a Hamiltonian operator.

In a crystal an electron may be regarded as 'free', or, as in a crystal orbital, a molecular orbital or an atomic orbital. The electrons in a 'free' state are subject to the crystal field and, along with all other components of the crystal, to any external fields. Electrons may also be coupled to the crystal lattice singly, as in excitons, polarons, and magnons, or in pairs, as in superconductivity. If the set R(i) i=1,n of phenomena in which electrons are 'free', bound (in orbital states), or coupled to the lattice is considered then there are an associated set of energy states E(i) i=1,n. Energy transfer is possible between these states, subject to various symmetry, parity, conservation and quantum mechanical rules. The set of possible types of transition are those associated with the set of Cartesian products P(ij) = R(i) X R(j) i,j=1,n, and, the set of mechanisms, (in which a number of members of P may participate) is given by the set of linear combinations $L = \Sigma c(k).P(ij)$ (i,j,k=1,n) c(k)=1 indicating the presence of the kth member of set P(ij) in the mechanism and c(k)=0 its absence. That is, a distinct mechanism may involve an electron in a finite sequence of energy transfers the initial and final states of the mechanism being observable.

In a crystal the number of mechanisms which are 'viable' is a function of the molecular/ionic or complex structure of the crystal. In addition to the host material forming the bulk

of the crystal, dislocations, guest-impurity species and other point defects form an important constituent of the crystalline environment. In a sense, from the point of view of an electron, the host material may be regarded as an hierarchical environment, in which the order of the hierarchy is atomic, molecular, inter-molecular or 'free' or crystalline. Changes in energy in a hierarchical system, within and between levels leads to a spectrum of discrete lines and bands with various levels of fine and hyperfine structure. Quantum mechanical rules allow discrete energy changes whilst continuous variation in the environment allows a certain spread in values about these otherwise discrete values.

In addition to the internal environment external influences may be brought to bear, namely, electric, magnetic and strain fields, temperature and electromagnetic radiation. These influences may either directly affect the single electron behaviour or do so indirectly via the crystal lattice or in coupled phenomena jointly. The external influences may be applied both singly or in combination.

The principal means of exciting electrons is with photons. It is specific in the sense that the photon-electron interaction is a many-one (although predominantly one-one) phenomenon. Sound and ultrasonic vibration, piezo-electric and pyro-electric effects are utilized to a limited extent in spectroscopic studies. On the other hand temperature variation is very useful, magnetic fields split degenerate spin states and electric fields greatly affect conduction. Strain fields can break symmetry and allow otherwise forbidden transitions.

2.1.2 CRYSTAL AND MOLECULAR ORBITALS

Crystal orbitals are described in terms of molecular orbitals and these in turn in terms of atomic orbitals. Various models with differing approximations are in common use. The calculation of molecular orbitals usually follows a Hartree Fock or self consistent field (SCF) approach using linear

combinations of atomic orbitals (LCAO) with simplifying assumptions such as complete neglect of differential overlap (CNDO).

The Huckel Theory uses an LCAO approach

$$\psi_i = \Sigma_j C_{ij} \phi_j$$

ψ_i being the ith molecular orbital
ϕ_j being the jth atomic orbital

The constraint of total energy minimisation yields the set of Huckel equations

$$\sum_{i=j}^{n} [H_{ij} - ES_{ij}]c_{ij} = 0 , \qquad j=1,2,...n$$

where H_{ij} is the Hamiltonian of the orbitals i,j and S_{ij} is the overlap integral of the two orbitals i and j. Hoffmann (1963) extended the Huckel model by approximating the off-diagonal terms H_{ij} as

$$H_{ij} = 0.5k(H_{ii} + H_{jj}) S_{ij}$$

where a factor k has been introduced into Mulliken's (1949) approximation for the product of two charge distributions χ_i and χ_j

$$\chi_i \chi_j = 0.5 S_{ij} (\chi_i \chi_i + \chi_j \chi_j)$$

Hoffmann (1963) carried out calculations of the energy for various conformations of a number of molecules using Slater atomic orbitals and found that the conformation of that with minimum energy tends to be close to that obtaining. Energies for a selection of compounds studied here are given in Table 2.1.2.

Molecular complexes have been studied in a number of ways. Chesnut and Moseley (1968) used a Hoffmann extended Huckel model simplified to the extent that they used only the $2p\pi$ orbitals of the molecular orbitals. Their aim was to study the relative geometry of the pair of molecules in the complex. The intramolecular geometries were held fixed at the experimentally determined values whilst the molecular relative geometry was varied in such a way as to keep the molecular planes parallel. The π only approximation is satisfactory for molecular separations

> 2.5 Å. The calculations indicate local minima close to the experimentally observed geometry in most of the complexes studied.

Table 2.1.2

CONFORMATIONAL ENERGIES OF SELECTED COMPOUNDS

Formula	Molecule	Energy (eV)
C_6H_6	benzene	-525.068
$C_{10}H_8$	azulene	-1019.095
$C_{12}H_{10}$	biphenyl	-841.681
$C_{14}H_{10}$	anthracene	-1158.974
$C_{14}H_{10}$	phenanthrene	-1158.974

2.1.3 CHARGE-TRANSFER COMPLEXES

The 1-1 charge-transfer complexes consist of stacks of normally neutral alternating donor (D) and acceptor (A) molecules. The crystal chemical unit contains a number of such pairs. The planes of the D and A molecules are usually approximately parallel to each other and about 3.5 Å apart. There is a limited amount of charge transfer between one molecule and the other and the characteristic $\pi-\pi$ absorption in the visible part of the spectrum evidences this.

Mulliken (1952) introduced the simple concept of a wave-function, describing partial charge transfer between a donor-acceptor pair, as being a linear combination of the wavefunction of the members of the pair.

$$\psi_c = a\psi_{D+} + b\psi_{A-}$$

where a and b denote the extent of mixing of the orbitals,

$$a^2 + 2abS + b^2 = 1$$

and $S = \int \psi_0 \psi_1 dv$ given that the ground state N of a molecular complex A.B is $\psi_N = a\psi_0 + b\psi_1 + \ldots$

This is a description for an isolated pair of atoms. For a pair of molecules in a CT or EDA (electron-donor-acceptor) complex ground states and excited states may be written (Mayoh & Prout 1972)

$$\psi_G = a\psi_{DA} + b_i\psi_{iD+A-} \quad \text{for which } a^2 >> b_i^2$$

$$\psi_{CT'} = a'\psi_{DA} + b'_i\psi_{iD+A-} \quad a'^2 << b'^2_i$$

respectively. Mulliken's (1956) "Overlap and Orientation Principle" states that the dependence of the CT interaction on the relative orientation of adjacent plane-to-plane D and A molecules may affect their orientation. The stabilisation energy E_G of the ground state due to CT interaction is calculated using 2nd order perturbation theory. (Mayoh and Prout 1972).

$$E_G = \sum_{\psi_{D+A-}}^{all} \frac{\langle \psi_{DA} | H | \psi_{D+A-} \rangle^2}{(E_{D+A-} - E_{DA})}$$

The mixing coefficient b_i of each CT state into the ground state is given by

$$b_i = \frac{\langle \psi_{DA} | H | \psi_{D+A-} \rangle}{(E_{D+A-} - E_{DA})}$$

The matrix elements reduce to an integral in terms of molecular orbitals and these to integrals involving atomic orbitals. CT interactions only affect orientation when London dispersive, charge dipole, dipole-dipole, dipole-induced dipole interactions are insensitive to orientation as they are generally higher in energy than CT stabilisation energies. Mayoh and Prout (1972) have shown that the CT interaction of the ground state, cannot be used as a guide to either the energy, or orientation sensitivity of the total CT stabilisation of a complex, although the majority of the complexes studied, have a donor-acceptor orientation, in which the CT stabilisation energy, is nearly maximised.

2.1.4 INTERMOLECULAR CHARGE TRANSFER

Middlemiss & Santry (1974) have looked at the intermolecular charge transfer in more detail using a self consistent field

(SCF) model. The approximate SCF matrix equation for a molecular crystal is

$$FC = CE$$

where F is the Fock matrix for the entire crystal, C is the coefficient matrix for the expansion of the crystal orbitals in terms of the atomic orbital basis set and E is the orbital energy matrix. The crystal density matrix is built up with linear combinations of atomic orbitals, for individual molecules, grouped together, so that when the matrix is partitioned according to molecules, submatrices on the diagonal are termed intramolecular (denoted ${}^{RuRu}P$).

'The first order submatrix for the Ruth molecule is

$${}^{RuRu}_{P}{}^{(1)}_{\mu\mu} = 4 \sum_{i}^{occ} \sum_{k}^{vac} \sum_{u} {}^{RuRu}_{A}{}_{ki} \, {}^{u}_{C}{}^{(0)}_{\mu k} \, {}^{u}_{C}{}^{(0)}_{\mu i}$$

where ${}^{u}_{C}{}^{(0)}_{\mu k}$ is the molecular orbital coefficient for the μth atomic orbital in the kth molecular orbital localized on a molecule occupying the uth site of the Rth unit cell.'

$${}^{RuRu}_{A}{}_{ki} = {}^{RuRu}_{F}{}^{(1)}_{ki} / ({}^{u}_{\varepsilon}{}^{(0)}_{i} - {}^{u}_{\varepsilon}{}^{(0)}_{k}) , \quad i \neq k$$

$${}^{RuRu}_{A}{}_{ii} = 0$$

${}^{u}_{\varepsilon}{}^{(0)}_{i}$ is the ith zero order orbital energy for the uth molecule.

$${}^{RuRu}_{F}{}^{(1)}_{ki} = \sum_{\mu}^{u} \sum_{v}^{u} {}^{u}_{C}{}^{(0)}_{\mu k} \, {}^{RuRu}_{F}{}^{(1)}_{\mu v} \, {}^{u}_{C}{}^{(0)}_{vi}$$

where ${}^{RuRu}_{F}{}^{(1)}_{ki}$ is the first order change in the Ruth intramolecular Fock subatrix. The total first order change in the electron population of the uth molecule is zero. ${}^{u}_{Q}{}^{(1)}$ is given by the trace of ${}^{RuRu}P^{(1)}$

$${}^{u}_{Q}{}^{(1)} = 4 \sum_{\mu}^{u} \sum_{i}^{occ} \sum_{k}^{vac} \sum_{u} {}^{RuRu}_{A}{}_{ki} \, {}^{u}_{C}{}^{(0)}_{\mu k} \, {}^{u}_{C}{}^{(0)}_{\mu i}$$

$$= 4 \sum_{i}^{occ} \sum_{k}^{vac} {}^{u}u_{Ru}^{Ru} A_{ki} \sum_{\mu} {}^{u}u_{\mu k}^{(0)} C_{\mu i}^{(0)} = 0$$

The second order change is ${}^{u}Q^{(2)}$.

$$ {}^{u}Q^{(2)} = 2 \sum_{T} \sum_{y} \sum_{i}^{occ} {}^{y}u_{k}^{vac} \{ {}^{RuTy}A_{ki} \}^2 - 2 \sum_{T} \sum_{y} \sum_{i}^{occ} {}^{u}u_{k}^{vac} \{ {}^{TyRu}A_{ki} \}^2 $$

This is zero for Ru = Ty, that is for intramolecular terms, but non-zero for intermolecular terms. Thus intermolecular interactions provide the leading contributions to intermolecular charge transfer. So the circumstances in which charge transfer may occur can be summarised as follows.

(1) Between independent molecules of the same type within a chemical unit.

(2) Between molecules of different types as in a CT complex.

(3) When a structural distortion, such as is produced by an asymmetric vibration of the unit cell molecules, breaks the equivalence of these molecules. Such a charge transfer could make a significant contribution to the change of dipole moment associated with the vibrations.

Given that, subject to these conditions, inter and intra molecular charge transfer is possible, it is of interest to examine, how charge carriers will flow in crystalline materials. This can be measured macroscopically and described in terms of a diffusion model. As our understanding improves microscopic models are developed and these must give the same or better results than the macroscopic models.

2.1.5 RANDOM WALK THEORY FOR ELECTRONS IN CRYSTALS

The possible movement of charge carriers around a crystal can be studied by consideration of various aspects of random walks on periodic lattices. Montroll & Weiss (1965) have considered a number of the aspects in the general case where steps $\underline{s}$ of length $|\underline{s}|$ are made on a toroidal k-dimensional lattice with N^k lattice points $\underline{s} = (s_1, s_2, \ldots s_k)$. The

principal assumptions and results of this model are given here. The probability that a random walker is at step $\underline{s}$ after n steps is given by $P_n(\underline{s})$ and in view of the periodic boundary conditions

$$P_n(s_1 + j_1N, s_2 + j_2N, \ldots, s_k + j_kN) = P_n(\underline{s})$$

where the j's are integers. If $p(\underline{s})$ represents the probability that any step results in a vector displacement, $\underline{s}$, by a walker then the $\{P_n(\underline{s})\}$ satisfy the recursion relation

$$P_{n+1}(\underline{s}) = \sum_{\underline{s}'} p(\underline{s}-\underline{s}')P_n(\underline{s}')$$

The Fourier expansion of $p(\underline{s})$, termed the structure function of the walker, is

$$\lambda(2\pi r/N) = \sum_s p(\underline{s})e^{2\pi i \underline{r}.\underline{s}/N}$$

When walkers are conserved during the walk $\sum_s p(\underline{s}) = 1$ and $\lambda(0) = 1$. The random walk generating function

$$P(\underline{s},z) = \sum_0^\infty z^n P_n(\underline{s})$$

is used and so by substitution

$$P(\underline{s},z) = N^{-k} \sum_r \frac{e^{-2\pi i \underline{r}.\underline{s}/N}}{1 - z\lambda(2\pi r/N)}$$

Considerable development of this model leads to a number of results amongst which the following is of interest here.

The average number of distinct lattice points visited after n steps S is given for 1, 2 and 3 dimensional lattices by

1D $S_n \sim (8n/\pi)^{1/2}$

2D $S_n \sim \pi n/\log n$

3D $S_n \sim n/P(0,1)$

where the value P(0,1) depends on the lattice type and is ~ 1.4 for cubic lattices. These results are of interest in that crystalline materials often have anisotropic properties and where the degree of anisotropy is large the crystals may be best regarded as one or two dimensional materials. The relative

values of S_n given here can therefore be used as discriminators of dimensionality when the physical properties involve processes which can be described by a random walk.

2.1.6 BARRIERS TO ELECTRON MOTION

An underlying assumption made in random walk theory is that all sites are equally probable. However, in any molecular crystal with its hierarchical environment and lattice imperfections there are time and positional influences prevailing on an electron which may not allow equivalent lattice points to be equally attractive to it. In some instances an electron has its walk terminated - it is trapped. In other circumstances there may be barriers to certain lattice points. To cross these barriers thermal excitation or tunnelling may be necessary. Such behaviour has been examined by Chojnacki, Lorenz & Pigon (1973) in which they account for changes in resistivity, activation and current-voltage characteristics in a doped crystal. The barrier height is the ionisation energy of the donor (anion), and the barrier has a width spanning an unspecified number of unit cells. The conductance is the product of the probability of crossing the barrier and the barrier width l. The probability of crossing the barrier is the sum of the probabilities of jumping and tunnelling the barrier which gives the conductivity

$$\sigma \sim [\exp(-\varepsilon/kT)+(1-\exp(-\varepsilon/kT))(D^{+} - D^{-})]l$$

where ε is the effective height of the barrier, D^{+} and D^{-} are the transmission coefficients in the direction of the electric field and opposite to it. Values of l estimated using rectangular barriers in the model are of the order of 35 Å for various levels of dopant. This model assumes that the effective mass of the electron is its free rest mass. Barrier widths comparable to the intermolecular spacing are equivalent to a much greater effective mass (Fleming

1972).

2.1.7 ELECTRON INTERACTIONS

A further consideration is necessary when charge carrier motion is depicted as being a random walk process. There may be a large number of walkers who may interact, such interactions being called space charge effects. That is, the walkers may impose an ordering on each other, thereby reducing the random element of their individual behaviour.

Space charge effects, limited diffusion and trapping can be either utilized, or avoided if possible, in experiments designed to examine charge carrier motion.

2.1.8 HOPPING MODELS

A number of organic charge-transfer crystals have been studied in which mechanisms involving 'hopping' have been discussed. The theory for models describing this (Mott, 1969, Brenig, Dohler & Wolfle 1971) is based on the assumption of hopping processes between localised states distributed randomly in "energy-coordinate-space". This, (Brenig, Dohler & Heyszenau 1972) yields the following temperature dependence for three dimensional hopping

$$\ln\sigma(T) = \ln\sigma_o - (T_o/T)^{1/4} \quad \text{where} \quad T_o = \alpha^3/N_f.$$

N_f is the density of states at the Fermi level and 0.5α is an average range parameter of the wave function of the localised states. In the case of TCNQ complexes a two-dimensional hopping model gives reasonable agreement with the data. The behaviour is anisotropic and $T_o = \alpha_{//}\,\alpha_{\perp}/N_f$ where $\alpha_{//}$ and $\alpha_{\perp}$ are range parameters parallel and perpendicular to the chains of the complex. It is interesting that subsequently Ehrenfreund et al (1972) re-examined this data and showed that a one-dimensional hopping model fits it even better than the two-dimensional one. This highlights the attention being paid

to this class of material. It is clearly of interest to correlate the molecular structure of crystalline materials with their physical properties, particularly where the dimensionality of the physical processes differs significantly from three.

2.1.9 POLARONS

A moving charge carrier may interact with the crystal lattice and its vibrations. This can be described in terms of a polaron. In polar crystals, the interaction of an electron, with the polarization field generated by the lattice vibrations, increases the effective mass to m_l, the polaron effective mass (Sewell 1958).

A tight binding model describes the situation in which a high effective mass pertains. As phonons exhibit a band structure, their interactions with other charge carriers leads to a band structure for polarons. The effective mass is temperature dependent

$$m_l = m_l^o \exp(T/T_l) \text{ for } kT >> h\upsilon, hc/a$$

where h is Planck's constant, c the speed of light, k Boltzmann's constant and a, a lattice parameter. This equation describes the fact that the random thermal motion of the ions opposes the transfer of their mean positions. As a consequence of this the energy to induce current flow of polarons will exhibit this same temperature dependence.

2.2 EXCITONS

2.2.1 INTRODUCTION

In superconductivity pairs of electrons are attracted to one another via the crystal lattice and move in concert. An exciton on the other hand is a similar type of phenomenon but with one of the electrons replaced by a hole. A hole has some of the same properties as a positron - positive charge in particular - but the

recombination of an electron and a hole is a much lower energy process than an electron-positron interaction. A number of scientists are searching for a material which makes a transition to a superconducting state at ambient temperatures. The exact nature of such a transition is unknown but it would appear plausible that it could be from exciton to bound electron pair, or perhaps an ordering, of pairs of excitons, giving paired electrons and paired holes. The contribution of holes to superconductivity has not been widely reported nor perhaps investigated. If the transition is an ordering of excitons, resulting in paired electrons, then a new approach to this interesting search could be made.

Currently the electrical properties of organic crystals and charge-transfer complexes are under intensive investigation, in order to widen our knowledge of their electrical behaviour. It is becoming more widely recognised that charge carrier motion is the behaviour of electrons and holes both singly and jointly as excitons. Excitons can be classified as singlet or triplet, depending on their spin state. Their investigation and use as probes (Mohwald, Erdle & Thaer 1977) is accordingly carried out using the techniques of electron spin resonance (ESR).

2.2.2 EXCITON GENERATION

Excitons may be inherently present in a given crystalline material, but they may be generated by various techniques. In anthracene, which has been the most widely investigated organic compound in this field, triplet excitons (Avakien & Merrifield 1968) have been generated directly by absorption of 'red' light (ruby laser), by recombination of injected holes and electrons in the crystal, as well as by bombardment by X-rays, and high energy particles. Singlet excitons can be generated optically and a proportion of these decay into triplet

excitons by intersystem crossing. Such singlet excitons are generated by a double absorption of laser light (Singh et al. 1965), or by an intense xenon flash lamp. The delayed fluorescence observed where double-photon absorption dominates, is proportional to the fourth power of the incident laser intensity. The double-photon generation of excited singlets is a square dependent process, as is the bimolecular triplet-triplet annihilation resulting in the delayed fluorescence.

2.2.3 EXCITON DIFFUSION

In order to examine exciton diffusion, triplets are generated by irradiating a small area of the crystal, in such a way that during their lifetime a substantial fraction of them will have time to move outside the illuminated region, and, as a consequence to a region of lower excitation concentration. Such a decrease in concentration leads to a decrease in the subsequent luminescence intensity. Ern et al. (1966) carried out dynamic experiments in which the excitation was both temporally and spatially inhomogeneous providing a full test for the time-dependent diffusion equation. This gave a value of 2×10^{-5} cm^2/sec for the triplet exciton diffusion constant pertinent to the ab plane of anthracene crystals at room temperature. Determination of scattering time and r.m.s. exciton velocity yields a scattering length of about 0.1 Å, from which it may be concluded that exciton motion in anthracene, is best viewed as a hopping process making very strong interactions interactions with the lattice.

2.2.4 EXCITON MOBILITY

Excitons may be mobile or immobile and it has been shown (Haarer & Wolf 1970) that the exciton hopping frequency υ can be estimated from the line narrowing

(observed in ESR) according to

$$\upsilon_j = \frac{1}{\tau}\left(\frac{\Delta H^{im}}{\Delta H}\right)^2$$

where τ is the life-time of the triplet state and where ΔH^{im} and ΔH are the line widths of the immobile and the mobile triplet states, respectively. Such techniques as this enable comparison of exciton diffusion mechanisms in different crystals. Mohwald and Sackmann (1973 & 1974) have published results for biphenyl-TCNB and anthracene-TCNB, finding fundamental differences in the triplet exciton diffusion processes therein. Anthracene-TCNB triplet excitons perform a two-dimensional diffusion in the planes of the crystal containing the donor molecules. The exciton diffusion coefficient D is estimated according to

$$D = l^2 \upsilon_j/2$$

where l is the average distance between two donor molecules in the donor plane.

2.2.5 EXCITON INTERACTIONS

Triplet excitons may interact with each other giving an annihilation. They may also interact with charge carriers releasing trapped carriers and enhancing photoconductivity. Interactions with photons leading to photoconductivity have been measured by Holzman et al. (1967). The effects of magnetic fields on the rate of triplet-triplet annihilation have been studied (Merrifield 1968). The anisotropic behaviour is explained in terms of the nine possible spin states of a pair of triplet excitons, the rate of annihilation being proportional to the fractional singlet character of each state.

2.2.6 EXCITON TRAPS

Triplet excitons may be trapped by impurities (Lupien and Williams 1968) and by dislocations (Arnold, Whitten & Damask 1970). The existence of traps is demonstrated by

delayed fluorescence and triplet lifetime measurements. Dislocations are easily induced by bending the crystal. For an unbent sample at room temperature the fluorescence in anthracene is found to be proportional to the incident excitation intensity, which is in accordance with fluorescence arising from triplet-triplet annihilation. The dislocation density N is proportional to the crystal curvature r, and is given by $N = 1/rb$ where b is the Burgers vector, and it is found that the increase in the fluorescence decay constant is proportional to N. In anthracene four types of trap are postulated to exist and to fit the fluorescence data they have depths between 0.02 and 0.3 eV.

2.3 PHOTOCONDUCTIVITY

2.3.1 INTRODUCTION

Photoconductivity is an interesting phenomenon in that it has a number of very practical applications, principally in light metering devices. Its simplest description is the generation of an electric current in a solid upon incidence of a photon. Consider an organic crystal such as anthracene. Electrons need to be promoted to the highest level in the hierarchical environment, that is to crystal orbitals, or exciton states. So it is not surprising that to a first approximation there is a threshhold energy for photoconductance, of wavelength typically about 4000 Å, and that in the presence of different gases (Kepler 1960) - the molecules of which can form or cause to be formed exciton affecting defects - the photoconductivity is different. The absorption of the incident photons is not necessarily directly by the defects, nor the excitons, but in anthracene (Bree, Carswell & Lyons 1955) is by the anthracene molecules themselves, as the spectral dependence of the photo-current generated follows pretty much the anthracene absorption spectrum. Photoconductivity arises therefore as a two step process (Melz 1972), an electron excitation

to an excited state and thence to a continuum state. It is generally agreed (Hughes 1971, Melz 1972, Chance & Braun 1973) that the free carrier yield in anthracene is controlled by geminate recombination. In 1938 Onsager modelled geminate recombination. The predicted electric field dependence of the free carrier yield, for a spherically symmetric distribution of geminate pair configurations is linear and has a slope to intercept ratio

$$S/I = e^3/8\pi\varepsilon\varepsilon_o k^2 T^2$$

where ε is the high-frequency dielectric constant and ε_o the permittivity of free space. Batt, Braun & Hornig (1968) observed the $1/T^2$ dependence and the linear field dependence of the carrier quantum yield

$$\phi = A(T)[1 + (e^3/2Dk^2T^2)E]$$

Geminate recombination describes the immediate recombination of a proportion of the electrons and holes following excitation, the photocurrent being due to those which do not recombine. The electrons and holes with a separation of r diffuse with the distribution $g(r,\theta)$, the angle θ being the angle made by $\underline{r}$ with the electric field $\underline{E}$.

The photo-generation efficiency for a particular electric field E is

$$\phi(E) = \phi_o \int f(r,\theta,E)g(r,\theta)d^3r.$$

Melz (1972) studied photogeneration in the polymer trinitrofluorenone-Poly(N-Vinylcarbazole). A film of this substance was deposited on an anodized aluminium substrate, and exposed to light pulses of 4 μsec duration. In this experiment

$$\phi(E) = C\Delta v/eF$$

where C is the capacitance/unit area of film, Δv the potential drop due to the light impulses and F the photons/cm^2 due to one light pulse.

Chance & Braun (1973) have also observed low-field

yield reductions which can be completely understood in terms of the recombination of free carriers with the opposite sign, being trapped charges left behind in the excitation region. As electrons migrate across the crystal they take up a Boltzmann distribution n(x) near the crystal surface (x=0)

$$n(x) = (eE/kT)Ne^{-xeE/kT}$$

where N is the number of free holes/cm of irradiated crystal surface. At time t = 0 the free electron distribution can be assumed to be

$$C(x,0) = k_o e^{-k_o x}$$

where k_o is the absorption coefficient of the excitation light. At time t the differential equation governing the electron distribution is

$$dC(x,t)/dt = -\gamma n(x,t)C(x,t)$$

γ is the second order rate constant for the free electron-trapped hole interaction and n(x,t) the distribution of electrons at time t is given by

$$n(x,t) = NeE/kTe[-eE/kT(x+uEt)$$

This is arived at by, imagining, moving the distribution of holes through a stationary distribution of electrons at u, the speed of the electron mobility. Solution of these equations leads to a prediction in agreement with the observed quantum yields in the experimental range of the electric fields used.

Bergman and Jortner (1974) have made a review of photoconductivity in anthracene and studied its dependence on incident intensity over a range of wavelengths. The description of organic crystals must be hierarchical rather than in terms of 'narrow' conduction and valence bands. Frenkel exciton states and the band states only constitute the zero-order levels of the system. 'Coulomb interactions couple the exciton and band states, non-adiabatic intramolecular terms couple vibronic components

of exciton states which correspond to different electronic configurations, while nuclear coupling terms involving both intermolecular and intramolecular nuclear displacements will couple different vibronic components of a single electronic configuration of a neutral or a band state.'

In the wavelength region 4400 - 4600 Å one photon excitation yields stable singlet excitons from which charge carrier generation is either by exciton photo-ionization or exciton collisions. The charge carrier yield m vs I dependence varies as follows. In the region 4600 - 6120 Å two photon excitation takes place and the m vs I dependence is mechanism dependent. In the region 4600 - 6120 Å the dependence is quadratic for low light intensities and quartic for high intensities. These dependences can be assigned to the production mechanisms - autoionization of metastable excitons and collision ionization of excitons respectively. From 6180 - 6943 Å a cubic m vs I dependence is observed, attributable to photoionization of two-photon-excited singlet states. As the m vs I dependences vary it is not particularly meaningful to make m vs υ measurements across the experimental range, but rather it is better to examine the cross-sections for the various photogeneration mechanisms.

2.3.2 CHARGE CARRIER MOBILITIES

The mobilities of both holes and electrons in anthracene are of the order of $1 cm^2/V\text{-}sec$ at room temperature (Le Blanc 1961), and vary with the temperature as T^{-n}, $1 < n < 2$. To model carrier mobility a tight binding approximation is made using Bloch momentum eigenfunctions of the perfect crystal, and the bands for electrons and holes are anisotropic and of width ~ 0.56kT at room temperature. Models of isotropic carrier scattering may assume either (i) $\tau(\underline{k}) = \tau_o$ constant free time, or (ii) $\tau(\underline{k}) \times |\underline{v}(\underline{k})| = \lambda_o$ constant free path for which the components of the mobility tensor

μ_{ij} are $e\tau_o \langle v_i v_j \rangle / kT$ and $e\lambda \langle v_i v_j / |\underline{v}(\underline{k})| \rangle / kT$ where the v_i are the components of $\underline{v}$ and the brackets represent a statistical average over the band. The velocity v is defined by

$$h\underline{v}(\underline{k}) = \partial E(\underline{k}) / \partial \underline{k}$$

where $\underline{k}$ is the wave vector of the wavefunction ϕ_k.

These models lead to values for τ_o of the order of 1.5×10^{-12} sec and for λ of 30 - 80 Å. The drift mobility μ of electrons and holes may be measured by injecting charge-carriers into a crystal surface and measuring the time to traverse the crystal t.

$$\mu = d^2 / Vt$$

where d is the distance traversed and V the applied voltage. When continuous carrier motion occurs space-charge-limited currents may be observed, depending on the current density. If space-charge effects are to be studied then a continuous source of carrier generation is used, whereas if they are to be avoided then a pulsed source is used giving transient currents to study. Such excitation is commonly made by pulsed laser with pulses of duration < 5 μsec.

The measured drift velocities in anthracene (Kepler & Hoesterey 1974) do not show any deviation from a linear dependence on the electric field in the range 0 - 16×10^4 V/cm. The hole mobilities are 2.4 times greater then the electron mobilities.

2.3.3 MOBILITIES IN CHARGE-TRANSFER COMPLEXES

In the case of N-Isopropylcarbazole-Picryl chloride (NIPC) (Sharp 1967) the Picryl chloride is a good electron acceptor and acts as a trap. This is illustrated by comparison of mobilities in a 1% and 50% picryl chloride mixture with NI. The ratio of the linear densities of traps is 3.0 whilst the inverse ratio of the measured mobilities is 3.6, suggesting a simple hopping model with the time spent in traps being porportional to the trap strength. The temperature dependence is exponential,

$$\mu = \mu_o e^{E/kT}$$

the value of E determined yielding a trap depth of 0.1 eV. The space-charge-limited current for one carrier in a trap-free insulator is given by the expression (Rose 1955)

$$I = 4.4 \times 10^{-14} k V^2 / d^3 \text{ amp/cm}$$

where k is the dielectric constant of the insulator. The V^2 and $1/d^3$ dependences are obtained in NIPC at low voltages and high light intensities. At lower light intensities the space-charge-limited condition is alleviated and an ohmic behaviour is realized.

2.3.4 ELECTRON MOBILITY IN PHENANTHRENE PMDA

This has been studied in detail by Haarer, Mohwald & Castro (1975). They find a mobility of 10^{-2} cm /Vsec at room temperature and an activation energy of 880 cm^{-1}, with an exponential temperature dependence

$$\mu = \mu_o e^{-\Delta E/kT}$$

in the experimental range $250 < T < 450^{o}K$. The magnitude of μ_o is anisotropic, its value when being measured parallel to the stack axis being approximately three times that measured perpendicular to the stack axis. The anisotropic features of this material can be attributed to the intermolecular interaction along the stack axis being considerably larger than the interaction perpendicular to the stack axis. Such features are triplet exciton energy transfer and charge-carrier transport. Haarer & Mohwald (1975) report a field-induced charge-carrier trapping process, and explain the magnitude of the electric field at which this occurs in terms of the quasi-one-dimensional nature of phenanthrene PMDA.

The application of a hopping model as used by Kepler & Hoesterey (1974) for anthracene seems justified. In a system with deep traps the mobility decays exponentially with time and the characteristic decay time is called the CC-trapping time. In phenanthrene PMDA the observed trapping processes follow a single exponential decay with a constant decay time perpendicular to the stack axis, and with a decay time which gets shorter at higher

fields along the stack axis. This field dependent reduction of the CC-trapping time is referred to as field induced trapping.

2.4 ESR SPECTROSCOPY OF CHARGE-TRANSFER COMPLEXES

The so-called weak CT-complexes, which are non-ionic in their ground states, contain considerable ionic contributions to their lowest excited singlet and triplet states. The phosphorescent spectra of these states are generally very broad and difficult to interpret, so, for observations of triplet behaviour it is more appropriate to use ESR techniques. They enable measurement of the dipolar interaction of the triplet electrons as characterised by the ZFS-parameters (zero field splitting) D and E. The dipolar interaction strongly depends on the distance between the two unpaired spins. Such measurements provide a technique to establish the charge-transfer character of triplet states. When the triplet molecules are delocalized, over more than one molecule, the D-value is significantly reduced. Mohwald and Bohm (1976) report measurements on naphthalene tetracyanobenzene N-TCNB crystals doped with different guest acceptors. In the case of the guest molecule hexacyanobenzene (HCNB) the hyper-fine splitting (Hfs) observed, is shown to be due to the α and β-protons of only one naphthalene molecule, with coupling constants of 1.9 and 2.2 Gauss respectively corresponding to a CT-character of 33%. This indicates a breakdown of the inversion symmetry in the triplet state, of the crystalline complex, the most probable explanation for this being, that the exciton-phonon interaction tends to stabilize in an asymmetric triplet state.

In the case of N-TCNB doped with pentacyanotoluene (PCNT) the Hfs are also well resolved and the CT-character is 26%. The complex Napthalene-s-trinitrobenzene (TNB) forms a trap in the N-TNB doped crystals described by the ZFS parameters $D = \pm 0.0670 cm^{-1}$; $E = \mp 0.0134 cm^{-1}$; $D^{*} = 0.0709 cm^{-1}$ which are rather high for a CT-complex, indicating a triplet state of low polarity. The Hfs shows 25 lines due to the coupling of three equal nitrogen atoms with three equivalent protons.

Napthalene-Chloranil shows an absorption and emission line, but without any resolvable Hfs, indicative of a very short triplet lifetime (< 1ms) so that the Boltzmann equilibrium is not established among the triplet sublevels. Using the D-value of chloranil the CT-character obtained is 76%, that is, extremely polar.

The Biomolecules riboflavin and flavin-adenosine dinucleotide, which were also studied as guests, show small Hfs, indicating an only slight interaction with the host donor napthalene, suggesting thereby that CT-crystals are suitable matrices, in which to study ESR-spectra of large oriented molecules.

Dalal, Haarer, Bargon and Mohwald (1976) have examined anthracene and phenanthrene as guest donor molecules in naphthalene TCNB. In the case of anthracene the degree of charge transfer (b^2), in the triplet state, is almost identical with that in the isolated molecule ($b^2 = 0.05$), whereas phenanthrene shows a significant degree of charge transfer ($b^2 = 0.47$).

Triplet excitons, have been examined in 1,4 dibromo-naphthalene crystals. Such crystals are stacked in linear arrays with the molecular planes being parallel, and so have similar properties to charge-transfer complexes. The molecules are translationally inequivalent, and so the ESR spectra of two pairs of lines, corresponding to this, yield only information on the exciton diffusion perpendicular to the stack axis. Mohwald and Sackmann (1973) have studied biphenyl-TCNB, in which the molecules are translationally equivalent (triclinic space group). This being so they cannot distinguish between behaviour parallel and perpendicular to the stack axis. They are able to conclude, that the lowest excited triplet state is a CT state, as the average ZFS parameter of the crystal triplet state is considerably smaller than the D-values of the donor and the acceptor, respectively. There is a strong narrowing of the ESR lines with increasing temperature above 77 ^{o}K, at which temperature the lines appear

to have been inhomogeneously broadened by the hyperfine interaction of the triplet state electrons with the nuclei of the donor and the acceptor. Above 77°K, at which temperature the triplet excitons are nearly immobilized, the exciton motion causes a random modulation of hyperfine interaction, leading to a motional narrowing of the ESR lines. Haarer (1969) has related the limiting line width ΔH_m at negligable exciton motion to the hopping frequency of the excitons by $\Delta H N^{1/2} = \Delta H_m$ where N is the number of hyperfine states seen by a diffusing exciton during its lifetime. Anthracene-PMDA (Haarer and Karl) has D and E values which clearly indicate that the ESR signal is due to the locally excited donor molecule (anthracene), rather than a CT triplet state. The ESR spectrum has both emissive and absorptive lines indicating a high degree of spin polarization.

ESR has been used by Erdle and Mohwald (1977) to investigate an orientational phase transition of anthracene in the CT-complex anthracene-TCNB. Above 196°K there is a libration of $\pm$ 9° by the anthracene, which freezes in during the transition, the crystal splitting into two sublattices. The triplet exciton being solely located on the anthracene molecule is a good indicator. At high temperatures a single narrow line is observed, which, at lower temperatures (<196°K) has split into broad lines corresponding to the two differently oriented sublattices. The phase change has both first and second order components and is described by an even function of the sixth order.

CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 PRELIMINARY CRYSTALLOGRAPHIC STUDIES

For each compound in a preliminary study, approximate cell constants were obtained using a precession camera, the crystal being mounted on a fine glass fibre using vaseline or araldite. This enabled examination of zero level and upper level reciprocal lattice nets to establish the space group symmetry. Nicely shaped single crystals were selected in each case particular care being taken to avoid twinned crystals. The crystal dimensions of the crystal chosen for data collection were measured, and its faces indexed, for purposes of absorption correction calculations, should they prove necessary.

3.2 DIFFRACTOMETER DATA COLLECTION

A suitable crystal was selected and two reflections, identified on a precession photograph, were located with the diffractometer thereby roughly establishing the crystal orientation. Subsequently, at least 12 higher angle reflections of reasonable intensity were located by rapidly accumulating intensity data from a thin shell of the reciprocal lattice.

These were then accurately centred using a 5.0 mm diffracted beam collimator (DBC) under the control of the computer and least-squares refinements of the cell constants and the orientation matrix carried out.

The tube take-off angle was always maintained at 3.0^{o} and tube alignment procedures (Furnas 1957) were such as to obtain an X-ray beam of uniform intensity in the various equivalent positions in which reflections can be measured. The crystal mosaicity was measured by making open-counter ω scans using strong, low angle reflections. If the peak was split or too broad the crystal was rejected.

The θ-2θ scan technique under computer control was

used to collect the intensity data. The incident beam was filtered using the appropriate β filter. Symmetric step scans, centred on the reflection's position calculated using the wavelength of the X-radiation, were carried out along with stationary counts of background radiation at both ends of the step scan. The total time for each background count was generally set to be half that of the integrated step scan. The crystal to DBC distance was 23 cm and all intensity data were collected using a 5.0 mm DBC.

When coincidence losses were significant the reflection intensity was re-measured with the incident beam being attenuated by suitable metal foils. These were calibrated at the end of the data collection by making long measurements of selected high intensity reflections. The calibration obtained varied slightly between crystals of different compounds.

Specific details and any changes or modifications are given in the discussion of the individual structures in later chapters.

3.3 DATA PROCESSING

The method of data processing was similar to that of Corfield, Doedens and Ibers (1967). Throughout the scan range, of any given reflection, background scattering is considered to be a linear function of θ. The measured intensity and estimated standard deviation are then formulated as

$$I = C - 1/2(t_c/t_b(B_1+B_2))$$

$$\sigma(I) = [(C + 1/4(t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$$

where I = intensity

C = scan count

B_1 = first background count

B_2 = second background count

t_c = scan counting time

t_b = background counting time

$\sigma(I)$ = estimated standard deviation in intensity

p (Grant, Killean & Lawrence 1969) is a factor introduced to avoid the overweighting of strong reflections and is of the order of 0.05.

The value of p was varied, so that the error in an observation of unit weight, showed minimal dependence on the magnitude of structure factors and Bragg angle, when refinement of the crystal structure was completed (Cruikshank 1965). The weighting function used in the analyses was

$$w = 4F_o^2/[\sigma(F_o^2)]^2$$

where F_o is the observed structure factor and $F_o^2 = kI$ where k is a constant for all reflections.

When equivalent reflections were observed, or the same one repeatedly observed for some reason, the estimated standard deviation esd $\sigma(F^2)$ was taken either as the average of the individual esd's, or, as a value estimated from the range of intensities of equivalent reflections, whichever was larger. Finally all esd's were multiplied by $(N/OBS)^{1/2}$, where N was the standard number of equivalent reflections measured, and OBS was the number actually recorded (Robinson & Ibers 1967).

Absorption corrections, where they proved necessary, were applied by using an analytical integration program ABSORB Templeton and Templeton (1973). Input to the program utilises perpendicular distances of crystal faces to an arbitrary origin in the crystal and the Miller indices of those bounding faces.

CHAPTER 4

SOLUTION AND REFINEMENT PROCEDURES

4.1 INTRODUCTION

Structures described in this thesis were solved by direct methods and Patterson techniques, and were refined by least-squares. Details of the methods used are outlined in this chapter whilst any details peculiar to individual structures are discussed later.

A crystal structure consists of an ordered set of atoms of various masses arranged in space, with certain periodicities defined by unit cell parameters. Generally the symmetry operations of the space group relate the asymmetric units within the unit cell to each other. Crystallographic description, is usually confined to the unit cell, and primarily to the asymmetric unit.

4.2 ELECTRON DENSITY AND STRUCTURE FACTORS

The electron density is given by:

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l |F(hkl)| e^{-2\pi i(hx+ky+lz)} e^{i\alpha}$$

where $|F(hkl)|^2 = \sum_i f_{oi}^2 e^{-B\sin^2\theta/\lambda^2}$, F(hkl) is defined as the structure factor for the reflection from plane hkl, and f_{oi} is the scattering factor of atom i at rest.

$B = 8\pi\overline{u^2}$ is the isotropic temperature factor.

u is the root-mean-square amplitude of vibration.

θ is the angle of incidence of the X-rays.

α is the phase angle (value 0 or π in centro-symmetric structures).

The electron density of each atom is represented as being spherically symmetric about its nucleus. Vibrational motion may be represented by a single parameter B as isotropic motion, or by six parameters describing an ellipsoidal anisotropic motion.

The measured intensities are proportional to $|F(hkl)|^2$ whilst the phase changes on reflection are not measurable. The phases are functions of the atomic positions and their elucidation is a primary problem in crystallography.

4.3 PHASE DETERMINATION

4.3.1 PATTERSON METHODS

A formulation useful in determining atomic positions is the Patterson Function (Patterson 1935).

$$P(u,v,w) = \int_0^1 \int_0^1 \int_0^1 \rho(x,y,z)\,\rho(x+u,y+v,z+w)\,V dx dy dz$$

where u,v,w is a point in Patterson-space and x,y,z a point in crystal-space. (V is the crystal volume). This formulation can be written in terms of a Fourier series.

$$P(u,v,w) = \frac{1}{V} \sum\sum\sum_{hkl} |F(hkl)|^2 e^{-2\pi i(hu+kv+lw)}$$

This expression can be evaluated at any point u,v,w since it is solely dependent on I(hkl) and independent of any phase angle. Its topological features are interpreted in the following manner:

1. The magnitudes of local maxima are proportional to the product of the numbers of electrons in the pairs of atoms between which the vectors are formed.
   At the origin there are the contributions of N vectors (1 from each of the N atoms to itself). The remaining maxima consist of two sets of N(N-1)/2 peaks related to each other by a centre of symmetry.
   As the density of peaks in a Patterson map is N times that of the molecular structure it represents, peaks often overlap and are not easily resolved. Their resolution can be improved by "sharpening". In a sharpened model the atoms are regarded as charges of equal value, located at particular points.
2. Local maxima represent interatomic vectors.
   The interatomic vectors fall into two classes, intra-molecular and intermolecular. The intermolecular vectors

can be further classified as to whether or not they are characterized by a difference between the symmetry operations of the real space group. Those that are, are termed Harker vectors. Harker vectors can be used to determine atomic coordinates, and, as a consequence, phases. In practice the Patterson peaks of greatest magnitude, representing vectors between the heavier atoms of a structure, are regarded as the most reliable. In a centrosymmetric structure the structure factor

$$F(hkl) = \Sigma f_j e^{-B_j \sin^2\theta/\lambda^2} \cos 2\pi(hx_j + ky_j + lz_j)$$

If atom m is a heavy atom f_m is much larger than f_j $(j \neq m)$ and then

$$F(hkl) \sim f_m e^{-B_m \sin^2\theta/\lambda^2} \cos 2\pi(hx_m + ky_m + lz_m)$$

That is, the sum is dominated by a single large term. The sign, and hence phase of F(hkl) is determined by the sign of $\cos 2\pi(hx_m + ky_m + lz_m)$. This approximation defines, what is known as, the heavy atom method.

3. The Patterson map is comprised of N images of the molecular structure, each displaced different distances from the true molecular site.

   Once one atom position is obtained analytically, using Harker peaks for instance, then the translation of the Patterson map, by a vector consisting of that atom's coordinates, will bring one of the N images to the true molecular position. This is known as a method of superposition.

In summary, the measured intensities determine the Patterson peak distribution and the intermolecular vectors thereby obtained, can enable the establishment of atomic positions and structure factor phases.

4.3.2 BASIS OF STATISTICAL METHODS

In the Heavy Atom Method use is made of an approximation in which one large term dominates a summation. This concept of a limited number of terms dominating a summation is also used in other phase determining techniques.
Bochner and Chandrasekharan (1949) have shown that for structure factors:

$$F(x^2) = \frac{1}{V} \sum_{h'k'l'} \sum \sum F(x)_{h-h',k-k',l-l'} F(x)$$

Sayre (1952) realised that the electron density function $d(x)$ and its square $d^2(x)$ are very nearly alike in shape and that it is possible to write

$$F(p^2)_{hkl} = S_{hkl} F(p)_{hkl}$$

where S_{hkl} is a function to account for the change in shape.

Whence $F(p^2)_{hkl} = \frac{1}{V} S_{hkl} \sum_{h'k'l'} \sum \sum F(p)_{h-h',k-k',l-l'} . F(p)_{h'k'l'}$

In particular, if, for h' = h", the values of $F(p)_{h-h",k-k",l-l"}$ and F(h"k"l") are large, then their product will tend to dominate the summation and so the phase of F(hkl) is in the main determined by them. The phase determining technique based on this equation is an iterative process, successive steps determining phases which are used to help determine further phases. Reliable methods have been developed, employing various approximations, and incorporating statistical techniques which are used to indicate that certain phases are true.

4.4 STATISTICAL METHODS IN PRACTICE

4.4.1 INPUT DATA

Normalised structure factor magnitudes $|E|$ known as E values are used, and are calculated in such a way that $\langle |E^2| \rangle = 1$. They are defined by the expression:

$$|E| = \left(\frac{\exp(A_o + A_1 \sin^2\theta)^{1/2}}{\tau \Sigma f_i^2 \sin\theta/\lambda} \right) |F_o|$$

Where $|F_o|$ is the measured structure factor, and f_i the atomic scattering factor, A_o and A_1 being defined by the Wilson Plot Method (Wilson 1942) using the expression:

$$\log_e \frac{<\Sigma_R m \tau \Sigma_N f_i^2 \sin\theta/\lambda>_q}{<\Sigma_R m |F_o|^2>_q} = A_o + A_1 <\sin^2\theta>_q$$

Here R is the number of reflections in range q, m is the multiplicity and τ is a factor to allow for systematic absences. Overall temperature (B) and scale (k') factors are obtained as

$$B = A_1 \lambda^2/2$$

$$k' = \exp(A_o/2)$$

4.4.2 USE OF MULTAN

Program MULTAN (Main, Woolfson & Germain 1971 & 1974) was used. The crystal structures described herein all have centrosymmetric space groups. MULTAN produces multiple solutions based on different sets of phases for a set of starting reflections. Frequently the solutions are the same, only apparently differing, due to different centres in the unit cell being taken as the origin.

Up to 500 reflections with E > 1.4 were used. In each case 2000 triplets ϕ_h, $\phi_{h'}$, $\phi_{h-h'}$ were sought and obtained. The set of phases having the best values for the figures of merit was always the correct set. MULTAN has three stages, SIGMA2, CONVERGE and FASTAN.

(i) SIGMA2 sets up all Σ_2 phase relationships.

$$\phi_h \sim \phi_{h'} + \phi_{h-h'}$$

and these are given weight

$$k_{hh'} = 2\sigma_3\sigma_2^{-3/2}|E_h E_{h'} E_{h-h'}|$$

where $\sigma_n = \sum_{j=1}^{N} z_j^n$

(ii) CONVERGE determines the origin defining reflections and a small group of other reflections which appear to provide a good starting point for phase determination.

(iii) FASTAN iteratively determines the final values for each set of phases using a refinement technique utilising a tangent formula:

$$\tan\phi_h = \frac{\sum_{h'} w_{h'} w_{h-h'} |E_{h'} E_{h-h'}| \sin(\phi_{h'} + \phi_{h-h'})}{\sum_{h'} w_{h'} w_{h-h'} |E_{h'} E_{h-h'}| \cos(\phi_{h'} + \phi_{h-h'})} = \frac{T_h}{B_h}$$

where $w_h = \tan(1/2\ \alpha_h)$

$$\alpha_h = |E_h|(T_h^2 + B_h^2)^{1/2}$$

4.5 MODEL BUILDING AND REFINEMENT

4.5.1 STRUCTURE FACTOR CALCULATION

For N atoms located at positions (x_j, y_j, z_j) the structure factor for the reflection from the plane hkl is

$$F(hkl) = \sum_{j=1}^{N} f_{oj}\, e^{-B_j \sin^2\theta/\lambda^2}\, e^{-2\pi i(hx_j + ky_j + lz_j)}$$

in which atom j has vibrational motion B_j, and scattering factor value f_{oj} appropriate to the angle of the reflection

$$\theta = \sin^{-1} \lambda/2d(hkl)$$

The tabulated vales for the scattering factors used were those of Cromer and Waber (1965) and for hydrogen those of Stewart, Davidson and Simpson (1965). For heavy elements in which the X-radiation falls near a natural absorption frequency, an anomalous phase change occurs and the scattering factor becomes complex. The total scattering

is then expressed as

$$f = f_o + \Delta f' + i\Delta f''$$

4.5.2 LEAST-SQUARES REFINEMENT

It is desirable to obtain atomic positions which minimise the differences between the structure factors calculated from them and the observed structure factors. Although the structure factors are not linear functions of the atomic parameters in the least-squares refinement the approximation is made that the equations are linear in the differences between the true values of the parameters, and the approximate values used. The quantity minimised is $w(|F_o|-|F_c|)^2$ where the weighting function

$$w = 4F_o^2/\sigma^2(F_o^2).$$

The conventional R factor R_1, and the weighted R factor R_2 are defined as

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$R_2 = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2)^{1/2}$$

4.5.3 REFINEMENT OF HYDROGEN ATOM PARAMETERS

Churchill (1973) surveyed recent crystallographic papers and concluded that 'refinement of positional (and thermal) parameters of hydrogen atoms can be a meaningful procedure and leads to self-consistent results even in the presence of heavy atoms'. Stewart, Davidson, and Simpson (1965) have shown that on theoretical grounds the use of free-atom spherically symmetric scattering factors for hydrogen, results in a reduction of 0.09 Å for C-H, N-H and O-H bonds determined by X-ray diffraction.

In this work hydrogen atom parameters have been refined in those structures where such refinement did not make the exercise too costly, otherwise they have been included in calculated positions.

4.5.4 DIFFERENCE FOURIER SYNTHESIS

The electron density is the Fourier Transform of the structure factors. Differences in the electron density distribution between the crystallographic model and reality can therefore be expressed throughout the unit cell in terms of the observed and calculated structure factors F_o and F_c as

$$\rho_{diff}(x,y,z) = \frac{1}{V} \Sigma\Sigma\Sigma_{hkl} (|F_o|-|F_c|)e^{i\alpha} e^{2\pi i(hx+ky+lz)}$$

This function reveals electron density as positive peaks. Its main use is to locate atoms that have not already been found and to assist in the improvement of the positioning of others. It requires a set of phases which are predominantly correct. The elucidation of further atomic sites leads to improvement of the set of phases. It yields positions which are good first estimates for refinement of atomic parameters by the method of least-squares.

CHAPTER 5

THE CHARGE-TRANSFER COMPLEX PHENANTHRENE PYROMELLITIC ACID DIANHYDRIDE

5.1 INTRODUCTION

In the complex phenanthrene-PMDA, phenanthrene acts as an electron donor and PMDA as an electron acceptor. The physical properties of this complex have been measured by Haarer & Mohwald (1975). In their studies they have encountered a new phenomenon which they have called field-induced charge-carrier trapping. Their discussion of the photoconductivity in terms of a hopping model enables them to argue that this new phenomenon is a consequence of the quasi one-dimensional nature of the phenanthrene-PMDA structure.

5.2 EXPERIMENTAL SECTION

Crystals were supplied by D. Haarer. They are yellow in colour and had been grown by the Bridgman method from chromatographed and zone-refined phenanthrene and PMDA (Mohwald & Castro, 1975). Preliminary precession photographs of these crystals exhibited monoclinic symmetry and the systematic absences 0k0 k odd, h01 l odd uniquely indicate the space group is $P2_1/c$. The density of the crystal was measured by flotation, $D_m = 1.44 g\ cm^{-3}$. Least-squares refinement of the cell constants as $\underline{a} = 7.046(3)$, $\underline{b} = 13.494(2)$, $\underline{c} = 19.396(7)$ Å, $B = 97.4(3)^\circ$ yields a calculated density of $1.44 g\ cm^{-3}$ with four molecular pairs in the unit cell.

Cu K_α radiation ($\lambda = 1.5418$ Å) was used, reflections being observed from a crystal of dimensions 0.5 x 0.6 x 0.8 mm having the planes (012), (012), (100), (012), (211), (012) as its bounding faces.

Data were collected for one quadrant of reciprocal space with $\theta < 57^\circ$. The intensities of the diffracted X-rays were measured with a 72 step single second 0.01° scan with 18 s background counts at each end of the scan. The normal attenuators used, at times

proved inadequate, as the crystal was a very powerful diffractor. Consequently additional foil was inserted into the diffracted beam and calibrated. The normal attenuation factors were 3.5, 9.5 and 33.3 and the foil gave an additional factor of 248. The intensities of three standard reflections were monitored every 100 reflections and the data scaled accordingly. Lorentz and polarization corrections were applied and of the unique reflections measured 1951 had intensities $>5\sigma$ and 2105 had intensities $>3\sigma$. No absorption corrections were made as test calculations showed them to be unnecessary, the range of possible corrections varying by no more than 5%. The linear absorption coefficient is 8.8 cm^{-1}.

5.3 STRUCTURE DETERMINATION AND REFINEMENT

As this complex is an all light atom structure direct methods techniques were used. 25 of the 30 non-hydrogen atoms were located by use of the program MULTAN (Main, Woolfson & Germain, 1971) using the 500 reflections with highest E values. The positions of the remaining five atoms were calculated and three cycles of refinement of positional and thermal parameters by full-matrix least-squares gave $R_1 = 0.203$. A difference Fourier calculation revealed additional electron density, near established atomic positions, indicative of anisotropic vibrational motion. Further refinement, with anisotropic thermal parameters for all non-hydrogen atoms, reduced R_1 to 0.092 and refinement of the H atom positions with isotropic thermal parameters finally gave $R_1 = 0.066$. Shifts in all parameters were less than 0.5 of their standard deviations in the final cycle of refinement.

A final difference Fourier synthesis revealed no anomalously large peaks.

5.4 DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of the complex consists of columns of alternately stacked molecules of phenanthrene and PMDA. Figures

5.4.1 and 5.4.2 define the atom labelling scheme used throughout this chapter. Figure 5.4.3 shows the spatial relations between the molecular pairs related by the symmetry elements of the space group. The x axis of the crystal is described as the stack axis and the phenanthrene-PMDA repeat distance along the stack axis is 3.5 Å whereas the perpendicular distance between these molecules is 3.36 Å. The angle between the normals to the molecular planes of a phenanthrene-PMDA pair, shown in Figure 5.4.3 is 4.11° and these same normals make angles of 15.52° and 14.35°, respectively, with the stack axis. The non-parallelism of the phenanthrene and PMDA molecules and the manner in which they overlap indicate localized interactions (Goldberg, 1975). The extent of such interactions is apparent in Figure 5.4.3. It is interesting to note that when a molecular pair is viewed in projection the O atoms in PMDA do not lie above regions of electron density (be they bonds or atoms) in the adjacent phenanthrene molecule. In fact, in this view five of the six oxygen atoms lie 'outside' the phenanthrene molecule. The sixth O atom lies centrally above one of the end phenyl rings in phenanthrene. This feature is common to complexes of PMDA with anthracene, naphthalene, perylene, pyrene (Herbstein, 1971) and fluorene (Evans & Robinson 1980a). It appears then that the C atoms and their concomitant H atoms are the atoms involved in the intermolecular binding and charge interactions.

The bond distances and angles calculated from the atomic coordinates (Table 5.4a) are given in Figures 5.4.1 and 5.4.2. These figures illustrate the anisotropic thermal vibrations of the atoms. Root-mean-square amplitudes of vibration are given in Table 5.4b, and structure factors in Appendix A1. There is no evidence of disorder in the structure.

The bond C(36)-C(46) is 1.442(3) Å in length - longer than any other C-C bond in phenanthrene. MO calculations (Banerjee & Basak, 1975) indicate that π-electron delocalization in phenanthroids is the main cause of this

lengthening rather than steric overcrowding of H atoms.

Figure 5.4.1

BOND DISTANCES AND ANGLES IN PHENANTHRENE

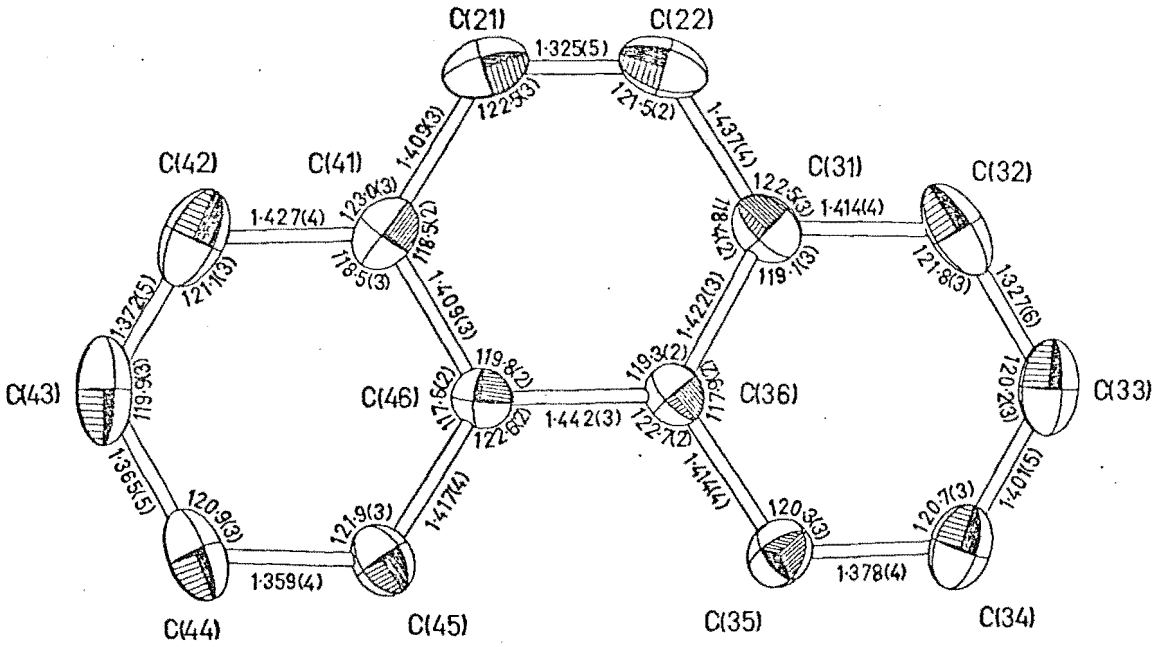


Figure 5.4.2

BOND DISTANCES AND ANGLES IN PMDA

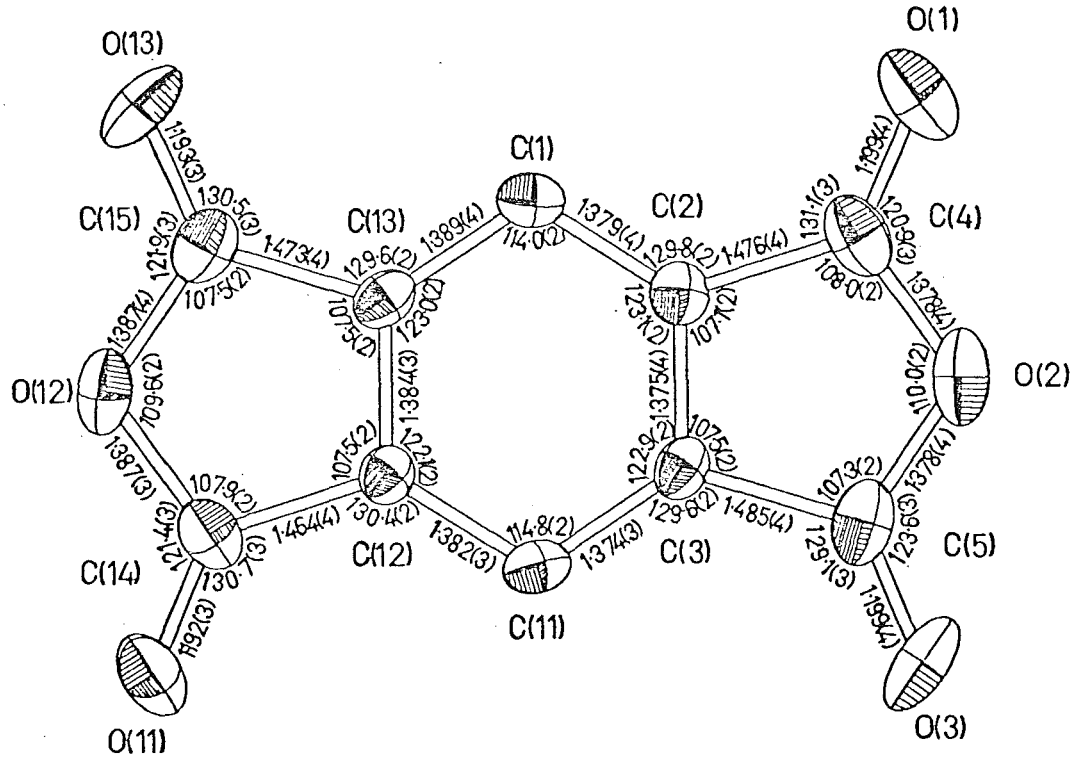


Figure 5.4.3

CRYSTAL PACKING OF PHENANTHRENE AND PMDA MOLECULES VIEWED DOWN THE STACK AXIS AND VIEWED EDGE-ON TO ONE OF THE PMDA MOLECULES

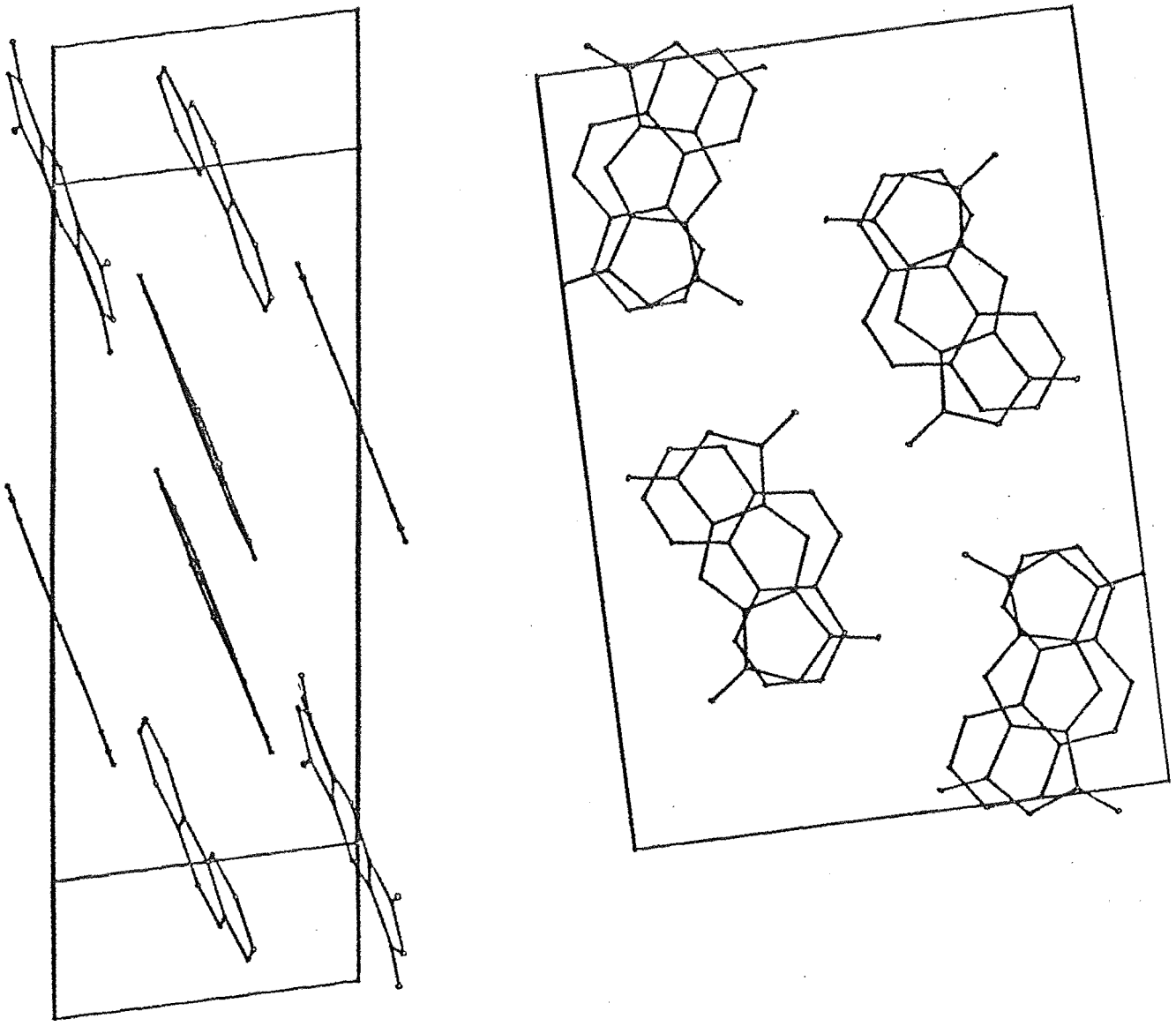


Table 5.4a

ATOMIC PARAMETERS FOR PHENANTHRENE PMDA

Atom	x	y	z	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0.0231(3)	0.3929(2)	0.6295(1)	0.0232(6)	0.0052(1)	0.0035(1)	0.0005(2)	0.0026(2)	0.0005(1)
C(2)	-0.0374(3)	0.3199(2)	0.5819(1)	0.0204(6)	0.0069(2)	0.0027(1)	-0.0002(2)	0.0024(2)	-0.0001(1)
C(3)	-0.0352(3)	0.2207(2)	0.5984(1)	0.0201(6)	0.0061(2)	0.0026(1)	-0.0015(2)	0.0025(2)	-0.0009(1)
C(4)	-0.1093(4)	0.3282(3)	0.5072(1)	0.0287(8)	0.0122(3)	0.0031(1)	0.0032(3)	0.0020(2)	0.0010(1)
C(5)	-0.1099(4)	0.1655(2)	0.5344(2)	0.0220(7)	0.0113(3)	0.0037(1)	-0.0015(3)	0.0027(2)	-0.0021(1)
C(11)	0.0244(3)	0.1857(2)	0.6642(1)	0.0246(6)	0.0046(1)	0.0037(1)	-0.0001(2)	0.0032(2)	-0.0001(1)
C(12)	0.0859(3)	0.2577(2)	0.7127(1)	0.0205(6)	0.0056(2)	0.0025(1)	0.0001(2)	0.0020(1)	-0.0004(1)
C(13)	0.0847(3)	0.3574(2)	0.6959(1)	0.0206(6)	0.0051(1)	0.0033(1)	-0.0002(2)	0.0030(2)	-0.0009(1)
C(14)	0.1613(4)	0.2487(2)	0.7863(1)	0.0284(7)	0.0088(2)	0.0029(1)	0.0034(3)	0.0014(2)	0.0006(1)
C(15)	0.1592(4)	0.4121(2)	0.7594(1)	0.0220(6)	0.0081(2)	0.0040(1)	0.0012(3)	0.0023(2)	-0.0017(1)
O(1)	-0.1365(4)	0.3993(2)	0.4702(1)	0.0502(8)	0.0162(3)	0.0038(1)	0.0047(3)	0.0014(2)	0.0028(1)
O(2)	-0.1505(3)	0.2342(2)	0.4820(1)	0.0316(6)	0.0155(2)	0.0028(1)	-0.0005(3)	0.0007(1)	-0.0019(1)
O(3)	-0.1315(3)	0.0780(2)	0.5261(1)	0.0367(6)	0.0113(2)	0.0063(1)	-0.0054(3)	0.0029(2)	-0.0051(1)
O(11)	0.1884(3)	0.1773(2)	0.8225(1)	0.0446(7)	0.0125(2)	0.0033(1)	0.0033(3)	-0.0006(2)	0.0016(1)
O(12)	0.2011(3)	0.3433(2)	0.8122(1)	0.0316(5)	0.0116(2)	0.0030(1)	0.0012(2)	0.0002(1)	-0.0020(1)
O(13)	0.1827(3)	0.4988(2)	0.7690(1)	0.0342(6)	0.0075(1)	0.0069(1)	-0.0013(2)	0.0030(2)	-0.0042(1)
C(21)	0.4553(4)	0.0894(2)	0.0734(2)	0.0266(7)	0.0089(2)	0.0042(1)	-0.0013(3)	0.0035(2)	-0.0027(1)
C(22)	0.5257(4)	0.0471(2)	0.1328(2)	0.0290(7)	0.0056(2)	0.0055(1)	0.0003(3)	0.0043(2)	-0.0008(1)
C(31)	0.5876(3)	0.1049(2)	0.1938(1)	0.0209(6)	0.0061(2)	0.0038(1)	0.0014(2)	0.0031(2)	0.0010(1)
C(32)	0.6642(4)	0.0615(3)	0.2578(2)	0.0281(8)	0.0099(2)	0.0055(1)	0.0025(3)	0.0046(3)	0.0035(1)
C(33)	0.7157(5)	0.1159(3)	0.3141(2)	0.0299(8)	0.0154(4)	0.0036(1)	0.0012(4)	0.0014(2)	0.0039(2)
C(34)	0.6979(4)	0.2193(3)	0.3112(2)	0.0305(8)	0.0139(3)	0.0023(1)	-0.0019(4)	0.0008(2)	0.0007(1)
C(35)	0.6262(4)	0.2658(2)	0.2501(1)	0.0261(7)	0.0083(2)	0.0025(1)	-0.0006(3)	0.0020(2)	-0.0001(1)
C(36)	0.5695(3)	0.2098(2)	0.1893(1)	0.0181(6)	0.0056(1)	0.0025(1)	-0.0006(2)	0.0023(2)	-0.0001(1)
C(41)	0.4368(3)	0.1941(2)	0.0657(1)	0.0104(6)	0.0083(2)	0.0027(1)	0.0003(2)	0.0027(2)	-0.0008(1)
C(42)	0.3617(4)	0.2406(3)	0.0019(1)	0.0250(7)	0.0157(3)	0.0022(1)	-0.0003(4)	0.0014(2)	-0.0009(1)
C(43)	0.3435(4)	0.3417(3)	-0.0030(2)	0.0289(8)	0.0122(3)	0.0036(1)	0.0021(3)	0.0022(2)	0.0025(1)
C(44)	0.4012(4)	0.3995(3)	0.0536(2)	0.0289(8)	0.0087(2)	0.0039(1)	0.0014(3)	0.0028(2)	0.0021(1)
C(45)	0.4760(4)	0.3585(2)	0.1151(2)	0.0266(7)	0.0062(2)	0.0031(1)	-0.0000(2)	0.0030(2)	0.0006(1)
C(46)	0.4943(3)	0.2545(2)	0.1239(1)	0.0179(5)	0.0063(2)	0.0023(1)	-0.0004(2)	0.0023(1)	-0.0001(1)
H(1)	0.022(3)	0.454(2)	0.612(1)	3.0(5)					
H(11)	0.018(4)	0.129(2)	0.674(2)	4.0(6)					
H(21)	0.403(5)	0.037(3)	0.036(2)	6.9(9)					
H(22)	0.525(4)	-0.038(2)	0.131(2)	5.0(7)					
H(32)	0.653(4)	-0.012(3)	0.251(2)	4.9(7)					
H(33)	0.752(4)	0.087(2)	0.350(2)	4.7(7)					
H(34)	0.716(4)	0.253(2)	0.350(2)	4.7(7)					
H(35)	0.598(4)	0.333(2)	0.245(2)	4.2(7)					
H(42)	0.319(4)	0.203(2)	-0.038(2)	3.8(6)					
H(43)	0.291(4)	0.369(2)	-0.046(2)	4.3(6)					
H(44)	0.393(4)	0.456(2)	0.045(2)	4.9(8)					
H(45)	0.510(4)	0.385(2)	0.159(2)	3.8(6)					

Thermal parameters are in the form of $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})]$

Table 5.4b

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION FOR PHENANTHRENE PMDA (Å)

C(1)	0.213(3)	0.225(3)	0.271(3)
C(2)	0.199(3)	0.243(3)	0.253(3)
C(3)	0.188(3)	0.213(3)	0.266(3)
C(4)	0.231(4)	0.257(4)	0.346(4)
C(5)	0.213(3)	0.243(4)	0.346(4)
O(1)	0.237(3)	0.345(3)	0.413(3)
O(2)	0.215(3)	0.281(3)	0.386(3)
O(3)	0.204(3)	0.298(3)	0.424(3)
C(11)	0.205(3)	0.222(3)	0.279(3)
C(12)	0.195(3)	0.228(3)	0.239(3)
C(13)	0.188(3)	0.219(3)	0.271(3)
C(14)	0.228(4)	0.245(3)	0.306(3)
C(15)	0.205(3)	0.251(3)	0.313(4)
O(11)	0.226(3)	0.335(3)	0.359(3)
O(12)	0.210(3)	0.278(2)	0.349(3)
O(13)	0.191(3)	0.288(2)	0.402(3)
C(21)	0.201(3)	0.253(3)	0.344(4)
C(22)	0.218(3)	0.253(3)	0.332(4)
C(31)	0.209(3)	0.222(3)	0.290(3)
C(32)	0.217(4)	0.254(4)	0.385(4)
C(33)	0.203(4)	0.272(4)	0.411(5)
C(34)	0.205(4)	0.272(4)	0.362(4)
C(35)	0.207(3)	0.255(3)	0.278(3)
C(36)	0.186(3)	0.225(3)	0.237(3)
C(41)	0.187(3)	0.244(3)	0.283(3)
C(42)	0.196(4)	0.249(4)	0.382(4)
C(43)	0.221(4)	0.263(4)	0.362(4)
C(44)	0.219(4)	0.261(3)	0.326(4)
C(45)	0.211(3)	0.244(3)	0.274(3)
C(46)	0.179(3)	0.227(3)	0.242(3)

CHAPTER 6

THE CHARGE-TRANSFER COMPLEX FLUORENE PYROMELLITIC ACID DIANHYDRIDE

6.1 INTRODUCTION

It seems that fluorene PMDA is the first fluorene containing charge-transfer complex to be studied. The structure of fluorene itself, a subject of controversy for twenty years, was finally resolved by Burns and Iball (1955). Fluorene is related to the carcinogenic dibenzfluorenes and benzanthracene, so it is interesting that structures of fluorene and benzanthracene with PMDA have been elucidated at points close in time. There is interest in relating carcinogenic properties to charge transfer properties as it is thought that complexing with DNA, RNA or a protein could play an important role in the mechanism of carcinogenesis (Foster, Scrimgeour, Iball & Williams 1975).

The physical properties of fluorene PMDA are as yet unpublished. The unusual packing found for the molecular pairs and the statistical disordering of the fluorene molecules may lead to electrical and spectral properties atypical of this class of compound.

6.2 EXPERIMENTAL SECTION

Crystals were supplied by D. Haarer. They are orange in colour and were grown by the Bridgman Method from chromatographed and zone-refined fluorene and PMDA (Haarer 1975). Preliminary precession photographs of these crystals exhibited monoclinic symmetry and the systematic absences 0k0 k odd, h0l l odd, uniquely indicate that the space group is $P2_1/c$. The density of the crystal was measured by flotation $D_m = 1.40 g\ cm^{-3}$. Least-squares refinement of the cell constants (using 12 centred reflections) as $\underline{a} = 10.146(2)$, $\underline{b} = 7.101(2)$, $\underline{c} = 13.004(2)$ Å, $B = 108.29(1)^\circ$ yields a calculated density of $1.44 g\ cm^{-3}$ with 2 molecular pairs in the unit cell. The implication of this is that each molecule has a centre of symmetry, which is possible

for PMDA, but not for fluorene, which therefore must be statistically disordered. The only other possibility is that one cell constant should be doubled. This possibility was ruled out by oscillation and Weissenberg photography using very long exposure times.

Cu K_α radiation (λ = 1.5418Å) was used. Data were collected for one quadrant of reciprocal space with $\theta < 76^\circ$ using an Hilger and Watts automatic diffractometer. The intensities of the diffracted X-rays were measured using an 80-step, single second, 0.01° scan with 20 second background counts at each end of the scan. Attenuators were used when the monitored pulses exceeded 8000/second. The attenuation factors were 3.44, 9.18 and 31.6. The intensities of 3 standard reflections were monitored every 50 reflections and the data scaled accordingly. Lorentz and polarisation corrections were applied and, of the unique reflections measured, 1177 had intensities >5σ and 1369 >3σ. No absorption corrections were made as test calculations showed them to be unnecessary, the range of possible corrections varying by no more than 5%. The linear absorption coefficient for Cu radiation is 8.96cm^{-1} for this compound.

6.3 STRUCTURE DETERMINATION AND REFINEMENT

Most of the structure was revealed by use of the direct methods program MULTAN (Main, Woolfson & Germain 1971) utilising those reflections having E > 1.06. PMDA is located with the unit cell origin at its centre of symmetry and its 8 unique atoms (1/2 molecule) were revealed immediately. On the other hand fluorene, which has no centre of symmetry, but is centred at (1/2, 0, 0) appeared as the superposition of two fluorene molecules - inverted with respect to each other. The orientation of the PMDA molecule was used to define a plane, with which it was expected the plane of the fluorene molecule would be parallel. A difference Fourier calculation, using phases determined by the PMDA molecule, in the plane in which the fluorene molecule was expected to lie, revealed two superimposed, inverted fluorene

molecules. Finding their locations was greatly facilitated by use of a line-printer electron density plot (see section 12.2). Figure 6.3a shows the superimposed molecules schematically. Figure 6.3b shows a line printer density map of the PMDA molecule in this structure. The refinements of the two 1/2 weighted fluorene molecules have resulted in some unusual C-C bond lengths in the 6-membered rings, because the atom C(32) in one of the superimposed molecules, and C(44) in the other are unresolvable. The parameters describing thermal motions of atoms in this area are of uncertain value. Considerable use was made of difference Fourier calculations between least-squares refinements, particularly for positioning the fluorene molecules. They also revealed that the vibrational motion of the atoms was anisotropic, particularly that of the oxygen atoms. Eventually least-squares refinement with anisotropic thermal parameters applied to all non-hydrogen atoms and isotropic parameters to hydrogen atoms converged with $R_1 = 0.055$. Shifts in all parameters were less than 0.2 of their standard deviation in the final cycle of refinement. Secondary extinction was observed to be present and the refined value of the Zachariasen extinction coefficient (Zachariasen 1963) is 0.11916×10^{-5}. A final difference Fourier synthesis revealed no anomalously large peaks.

6.4 DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Figures 6.4a and 6.4b are projected views of the two molecules PMDA and fluorene and serve to define the atom labelling scheme used in this chapter. Figure 6.4c shows spatial relationships between the molecules in the structure, emphasising both the stacking and interplanar angles between the molecules. Two features of this structure are worth special note, the molecular packing and the statistically disordered orientation of the fluorene molecules.

The structure of fluorene PMDA can be viewed in two ways.

Figure 6.3a

SCHEMATIC DIAGRAM OF SUPERIMPOSED FLUORENE MOLECULES

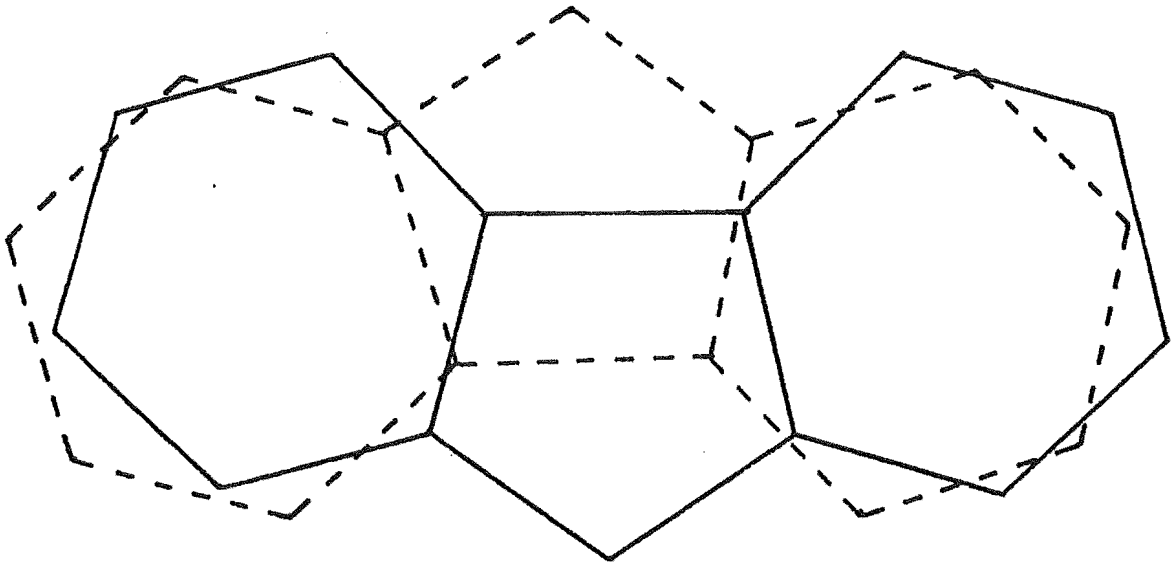


Figure 6.3b

LINE-PRINTER SHADED ELECTRON DENSITY MAP OF PMDA

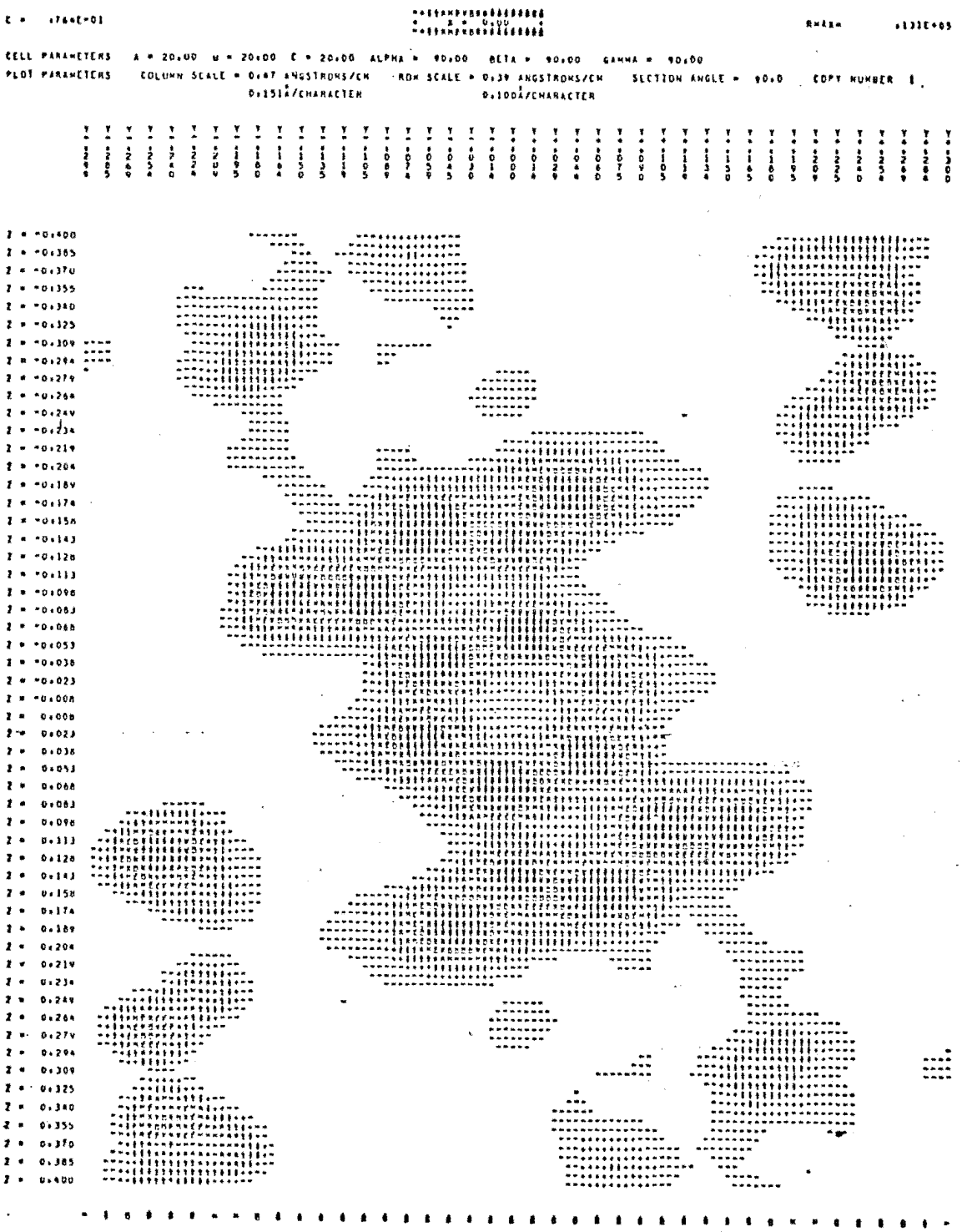


Figure 6.4a

BOND DISTANCES AND ANGLES IN FLUORENE

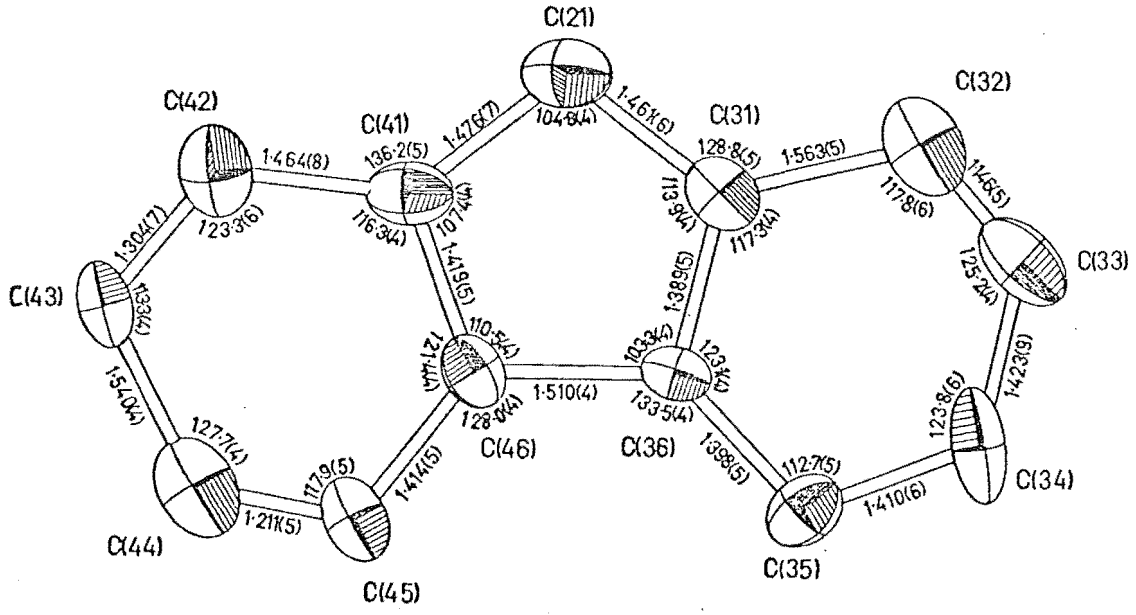


Figure 6.4b

BOND DISTANCES AND ANGLES IN PMDA

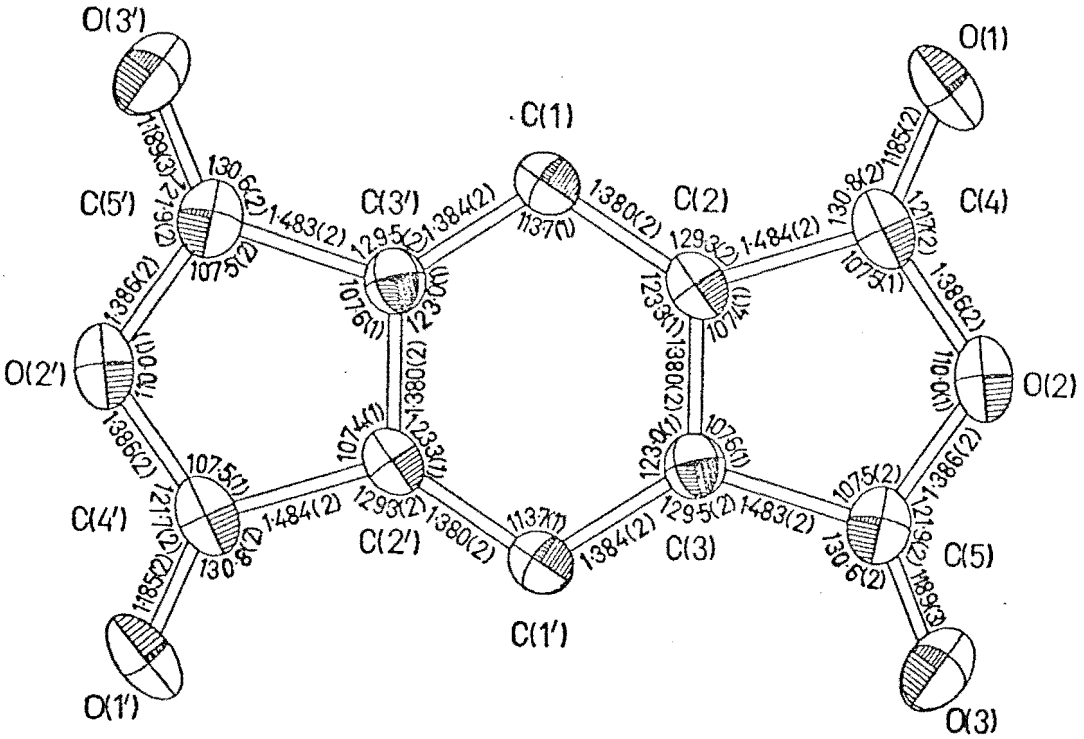
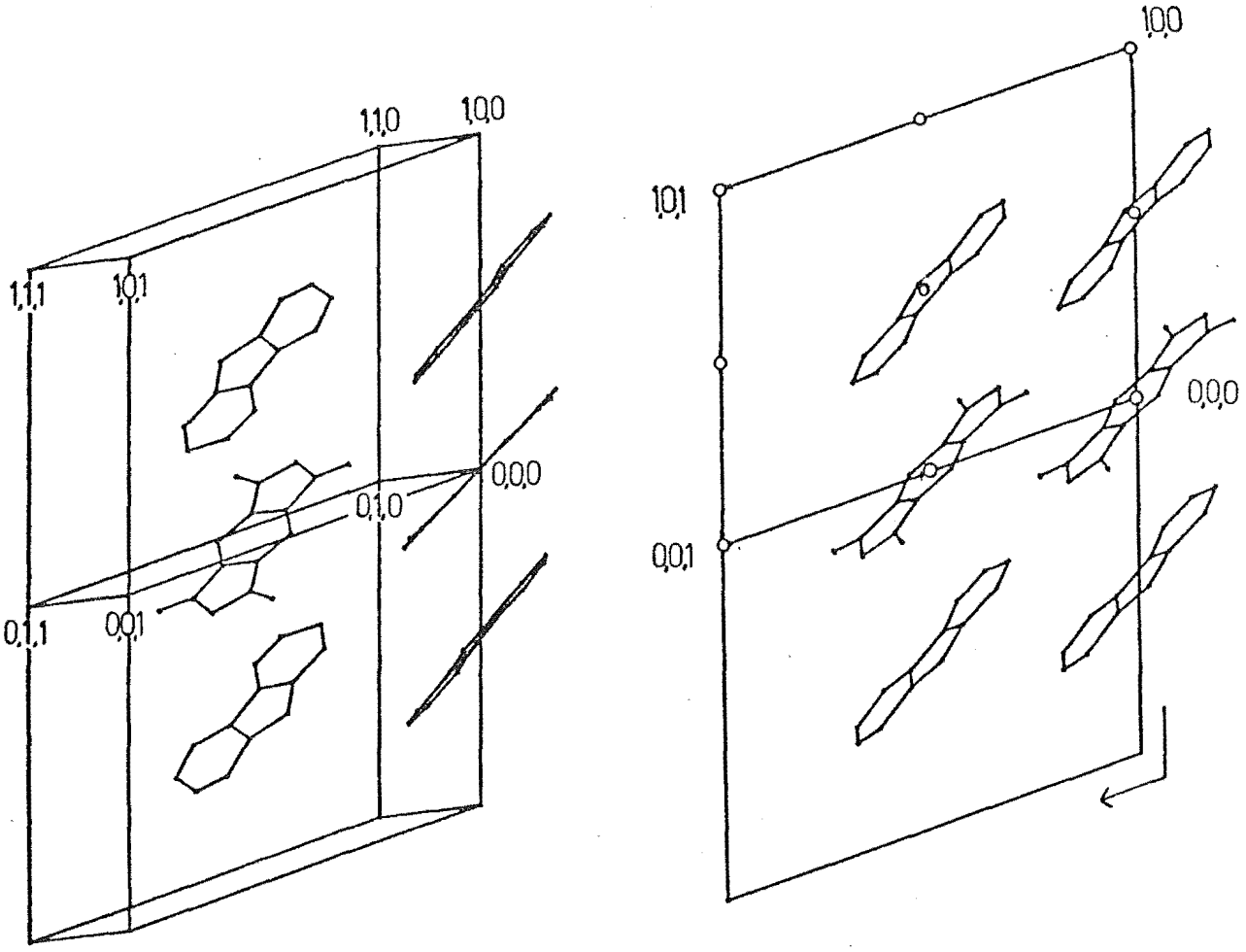


Figure 6.4c

VIEWS EDGE ON TO A FLUORENE MOLECULE AND PARALLEL TO THE y AXIS



As a charge-transfer complex of fluorene and PMDA molecules, stacked in the a direction, the donor and acceptor molecules are unusually far apart (5.07 Å). An alternative description is one in which there are separate fluorene and PMDA stacks along the b direction, the intermolecular stacking being the more usual distance of 3.522 Å (c.f. 3.5 Å Herbstein 1971). The average fluorene-PMDA interplanar distance is 4.46 Å. Atomic parameters are given in Table 6.4a, root-mean-square amplitudes of vibration in Table 6.4b and structure factors in Appendix A2.

The type of disorder obtaining in fluorene PMDA has been observed in at least four other compounds - azulene (Robertson, Shearer, Sim & Watson (1964), di-indenyliron (Trotter 1958), acepleiadylene (Hanson 1960) and 2 amino-4-methyl-6-chloro-pyrimidin (Clews & Cochran 1948). In all these compounds, except the last, there are five and six membered rings fused as in azulene, and in all except di-indenyliron the disorder relates to a centre of inversion. In hindsight it is interesting to note that Burns & Iball (1955) discounted such disorder when they examined the crystal structure of fluorene itself, whereas here, in the pure fluorene stacks, there is statistical inversion. This is, of course, also observed in the fluorene PMDA stacks and Figure 6.4c illustrates the case where reversal of the fluorene orientation has taken place in successive cells.

Table 6.4a

ATOMIC PARAMETERS FOR FLUORENE PMDA

Atom	x	y	z	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	-0.0130(2)	0.1817(2)	-0.0524(1)	0.0142(2)	0.0247(4)	0.0075(1)	-0.0013(2)	0.0035(1)	0.0011(2)
C(2)	-0.0510(2)	-0.0294(2)	0.0825(1)	0.0119(1)	0.0278(4)	0.0064(1)	-0.0025(2)	0.0032(1)	0.0000(2)
C(3)	-0.0631(2)	0.1444(2)	0.0330(1)	0.0120(2)	0.0243(4)	0.0072(1)	-0.0009(2)	0.0030(1)	-0.0008(1)
C(4)	-0.1152(2)	-0.0146(3)	0.1702(1)	0.0142(2)	0.0384(5)	0.0076(1)	-0.0031(3)	0.0045(1)	0.0009(2)
C(5)	-0.1367(2)	0.2707(3)	0.0877(1)	0.0147(2)	0.0309(5)	0.0100(1)	-0.0002(3)	0.0045(1)	-0.0031(2)
C(21)	0.4618(5)	0.2500(7)	-0.0234(5)	0.0163(5)	0.027(1)	0.0149(4)	0.0014(6)	0.0032(4)	0.0017(5)
C(31)	0.5819(4)	-0.1281(6)	-0.0505(3)	0.0115(4)	0.029(1)	0.0094(3)	-0.0002(6)	0.0020(3)	-0.0037(4)
C(32)	0.3336(2)	0.1803(5)	0.1283(2)	0.0151(3)	0.0501(9)	0.014(2)	-0.0024(4)	0.0032(2)	-0.0083(4)
C(33)	0.6852(5)	-0.0644(9)	-0.1834(5)	0.0144(6)	0.041(2)	0.0132(5)	0.0039(7)	0.0011(4)	-0.0099(7)
C(34)	0.6401(4)	0.126(1)	-0.1853(4)	0.0122(5)	0.074(3)	0.0088(3)	-0.0001(9)	0.0052(3)	-0.0062(8)
C(35)	0.5649(4)	0.1954(7)	-0.1189(4)	0.0142(5)	0.031(1)	0.0089(3)	-0.0009(6)	0.0020(3)	0.0041(5)
C(36)	0.5344(3)	0.0560(5)	-0.0540(3)	0.0108(4)	0.0168(8)	0.0081(2)	0.0021(4)	0.0018(2)	-0.0007(4)
C(41)	0.4600(4)	-0.1255(6)	0.0742(4)	0.0123(5)	0.022(1)	0.0126(4)	-0.0000(5)	0.0009(3)	0.0010(5)
C(42)	0.3919(5)	-0.144(1)	0.1575(4)	0.0137(5)	0.050(2)	0.0091(4)	0.0024(7)	0.0027(4)	-0.0004(6)
C(43)	0.3272(4)	-0.0062(7)	0.1872(3)	0.0119(5)	0.041(1)	0.0034(3)	0.0001(6)	0.0040(3)	-0.0044(4)
C(44)	0.3336(2)	0.1803(5)	0.1283(2)	0.0151(3)	0.0501(9)	0.014(2)	-0.0024(4)	0.0032(2)	-0.0083(4)
C(45)	0.3899(4)	0.2092(8)	0.0604(3)	0.0139(5)	0.036(1)	0.0101(3)	-0.0006(6)	0.0044(3)	-0.0056(5)
C(46)	0.4583(3)	0.0566(6)	0.0289(3)	0.0106(3)	0.029(1)	0.0077(2)	0.0013(5)	0.0023(2)	-0.0030(4)
O(1)	-0.1246(2)	-0.1264(3)	0.2352(1)	0.0225(2)	0.0535(5)	0.0097(1)	-0.0035(3)	0.0084(1)	0.0045(2)
O(2)	-0.1668(1)	0.1667(2)	0.1676(1)	0.0161(2)	0.0401(4)	0.0095(1)	-0.0006(2)	0.0064(1)	-0.0038(2)
O(3)	-0.1687(2)	0.4318(2)	0.0720(1)	0.0218(2)	0.0315(4)	0.0157(2)	0.0048(2)	0.0071(2)	-0.0033(2)
H(1)	0.021(2)	-0.305(3)	0.087(1)	3.7(4)					
H(211)	0.493(7)	-0.337(8)	-0.003(5)	8.(1)					
H(212)	0.614(6)	-0.312(7)	0.074(4)	7.(1)					
H(32)	0.68(1)	-0.37(1)	-0.134(8)	14.(3)					
H(33)	0.747(5)	-0.084(7)	-0.237(4)	5.(1)					
H(34)	0.649(5)	0.240(7)	-0.248(4)	6.(1)					
H(35)	0.538(5)	0.323(7)	-0.116(4)	5.(1)					
H(42)	0.407(5)	-0.251(8)	0.180(4)	6.(1)					
H(43)	0.292(6)	-0.073(9)	0.240(5)	7.(1)					
H(44)	0.288(4)	0.295(6)	0.141(3)	2.9(7)					
H(45)	0.388(4)	0.334(6)	0.035(3)	4.2(8)					

Thermal parameters are in the form of $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})]$

Table 6.4b

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION FOR FLUORENE PMDA (Å)

	Min	Int	Max
C(1)	0.229(2)	0.252(2)	0.266(2)
C(2)	0.216(2)	0.231(2)	0.274(2)
C(3)	0.233(2)	0.235(2)	0.254(2)
C(4)	0.225(2)	0.257(2)	0.319(2)
C(5)	0.245(2)	0.265(2)	0.303(2)
C(21)	0.256(5)	0.281(5)	0.353(5)
C(31)	0.227(4)	0.246(6)	0.305(4)
C(32)	0.259(3)	0.292(3)	0.396(3)
C(33)	0.243(5)	0.252(5)	0.408(7)
C(34)	0.204(6)	0.264(5)	0.443(8)
C(35)	0.234(5)	0.259(5)	0.316(5)
C(36)	0.196(5)	0.227(4)	0.267(4)
C(41)	0.234(5)	0.239(6)	0.338(6)
C(42)	0.249(5)	0.274(6)	0.359(6)
C(43)	0.204(5)	0.243(5)	0.334(5)
C(44)	0.259(3)	0.292(3)	0.396(3)
C(45)	0.234(5)	0.257(4)	0.333(5)
C(46)	0.220(5)	0.227(4)	0.292(5)
O(1)	0.211(2)	0.334(2)	0.381(2)
O(2)	0.223(2)	0.285(2)	0.333(2)
O(3)	0.248(2)	0.334(2)	0.355(2)

CHAPTER 7

THE CHARGE-TRANSFER COMPLEX THIANTHRENE PYROMELLITIC ACID DIANHYDRIDE

7.1 INTRODUCTION

This chapter describes the structure of a complex which appears to be the first involving thianthrene. PMDA plays its usual role of electron acceptor (Evans & Robinson 1980a). The structure of the folded thianthrene molecule was first determined by Lynton & Cox (1956) after Sutton (1955) had aroused their interest in the C-S bond geometry by pointing out that the sulphur atoms could use $d\pi$ as well as $p\pi$ orbitals in $\pi-\pi$ bonding. This type of complex, in which $d\pi$ orbitals may be involved in charge transfer processes, is apparently new. The non-planar conformation of thianthrene causes difficulties in describing the arrangement of molecules in this charge transfer-complex in terms of a specific stack axis.

Physical properties of this complex have yet to be published.

7.2 EXPERIMENTAL SECTION

Crystals were supplied by D. Haarer. They are reddish-orange in colour and had been grown by the Bridgman method from chromatographed and zone-refined thianthrene and PMDA (Haarer 1975). The lack of systematic absences and symmetry in preliminary precession photographs, as well as Wilson statistics, suggested the triclinic centrosymmetric space group $P\bar{1}$. The density of the crystal was measured by flotation $D_m = 1.50$g cm^{-3}. Least-squares refinement of the cell constants (using 12 centred reflections) as $\underline{a} = 11.128(1)$, $\underline{b} = 12.309(1)$, $\underline{c} = 7.334(1)$ Å, $\alpha = 99.716(5)$, $\beta = 82.617(5)$, $\gamma = 107.450(5)^{\circ}$ yields a calculated density of 1.54g cm^{-3} with two molecular pairs in the unit cell. All data given in this chapter relate to this unconventional cell. The conventional reduced cell constants $\underline{a} = 11.128$, $\underline{b} = 13.899$, $\underline{c} = 7.334$ Å, $\alpha = 92.67$, $\beta = 97.38$, $\gamma = 122.35^{\circ}$ can be derived from those used by application of the transformation

matrix $\bar{1}00/110/001$.

Cu K_α radiation (λ = 1.5418Å) was used. Data were collected for one hemisphere of reciprocal space with $\theta<57^\circ$. The intensities of the diffracted X-rays were measured using a 72-step, single second, 0.01° scan with 18 second background counts at each end of the scan. Attenuators were not required. The intensities of three standard reflections were monitored every 100 reflections and the data scaled accordingly. Lorentz and polarisation corrections were applied and, of the 2530 unique reflections measured, 1507 had intensities $>5\alpha$ and 1802 intensities $>3\alpha$. Test calculations showed that absorption corrections would be unnecessary as the range of possible correction factors required was no more than 7%.

7.3 STRUCTURE DETERMINATION AND REFINEMENT

The direct methods program MULTAN (Main, Woolfson & Germain 1971) was used, utilizing the 376 reflections having E > 1.4. Of the eight possible sets of phases the first two had the highest figures of merit. One of these had all phases the same whilst the other proved to be the correct set. Twenty-eight of the thirty non-hydrogen atoms were located using a Fourier synthesis based on the phased E values. The two remaining atoms were located using a difference Fourier calculation based on structure factors obtained following least-squares refinement of the established structural parameters. Refinement, with isotropic thermal parameters for the atoms, resulted in an agreement factor R_1 of 0.146. A difference Fourier calculation showed some evidence for anisotropic motion, particularly for the sulphur atoms. Using anisotropic thermal parameters the agreement factor R_1 reduced to 0.086. Refinement with hydrogen atoms having isotropic thermal parameters converged with R_1 = 0.073. Owing to the high number of variable parameters towards the end of the refinement procedure the least-squares calculations had to be done in blocks, and in order to help decide the order of refinement calculations of the standard deviations of the various

bond types within each molecule were carried out. The program BONDSTAT (see section 12.4) was used. Secondary extinction was detected and, in a final cycle of refinement, the value of the Zachariasen extinction coefficient (Zachariasen 1963) obtained was 0.16425×10^{-6} and R_1 reduced to 0.064.

A final difference Fourier synthesis revealed no anomalously large peaks.

7.4 DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of the complex consists of columns of alternately positioned thianthrene and PMDA molecules. Two PMDA molecules are present in the cell in crystallographically independent positions, about each of the centres of symmetry (0, 0, 0) and (1/2, 1/2, 1/2). The two thianthrene molecules are related by the space group centre of inversion. Figures 7.4a,b and c define the atom labelling scheme used throughout this chapter. Figure 7.4d shows the spatial relationships amongst the various molecules in the unit cell. The dihedral angle between the wings of the thianthrene molecule is 130.08°. This can be compared with 128° for thianthrene (Lynton & Cox 1956), 131.1° for 2,7-dimethylthianthrene (Wei 1971) and 138°38' for thianthrene dioxide (Hosoya 1966). The average C-S-C angle is 100.5° and the average C-S distance is 1.767 Å in excellent agreement with the values of 100.1° and 1.758 Å given by Lynton & Cox (1956) and the bond length is shorter than the sum of the covalent radii (1.812 Å; radii given by Pauling 1960).

The orientation of the PMDA molecules is influenced by the bent nature of thianthrene. Successive PMDA molecules are aligned with 'opposite ends' of the particular thianthrene molecule between them. The average distance between the parallel (aligned) portions is 3.51 Å and the angle between normals to their planes is 4.72°. Figure 7.4c suggests that the [111]

Figure 7.4a

BOND DISTANCES AND ANGLES IN THIANTHRENE

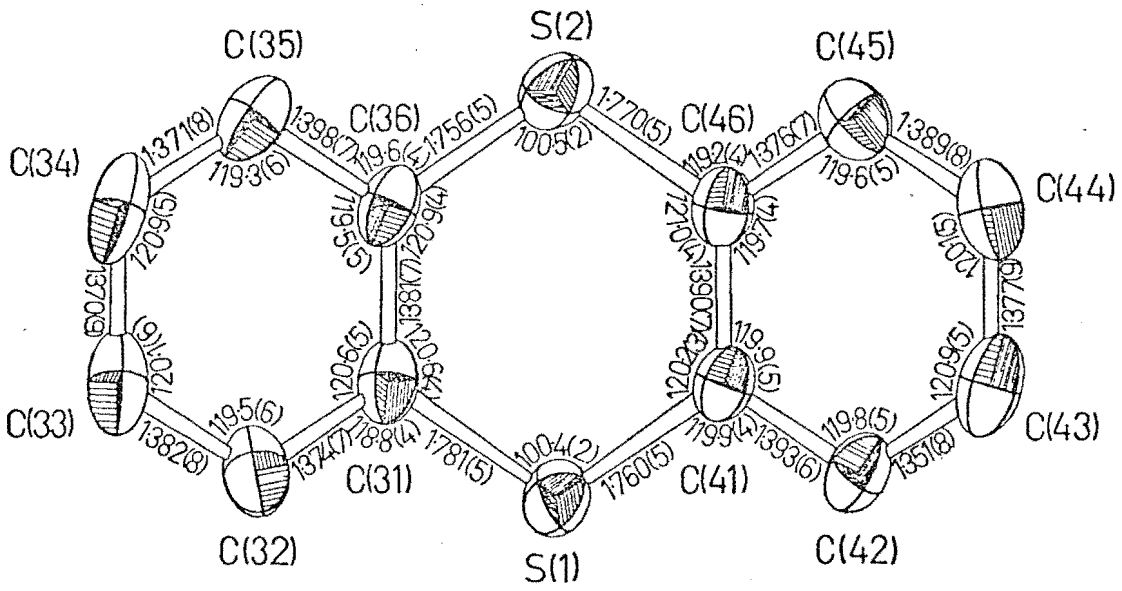


Figure 7.4b

BOND DISTANCES AND ANGLES IN PMDA (1)

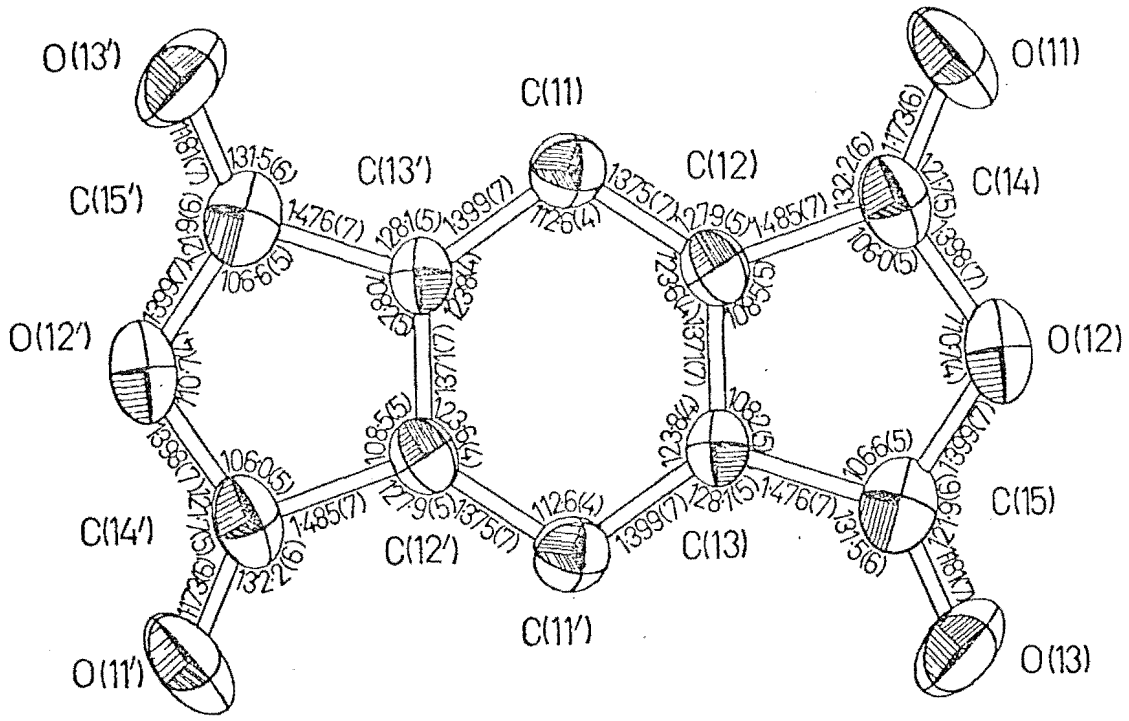


Figure 7.4c

BOND DISTANCES AND ANGLES IN PMDA (2)

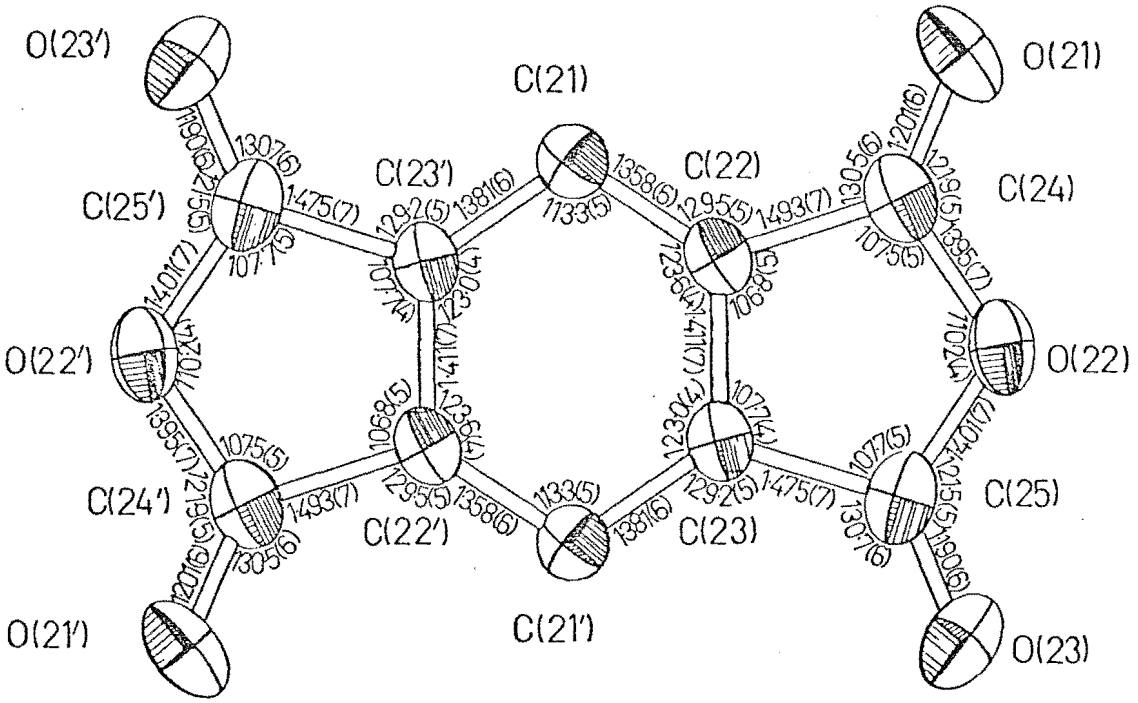
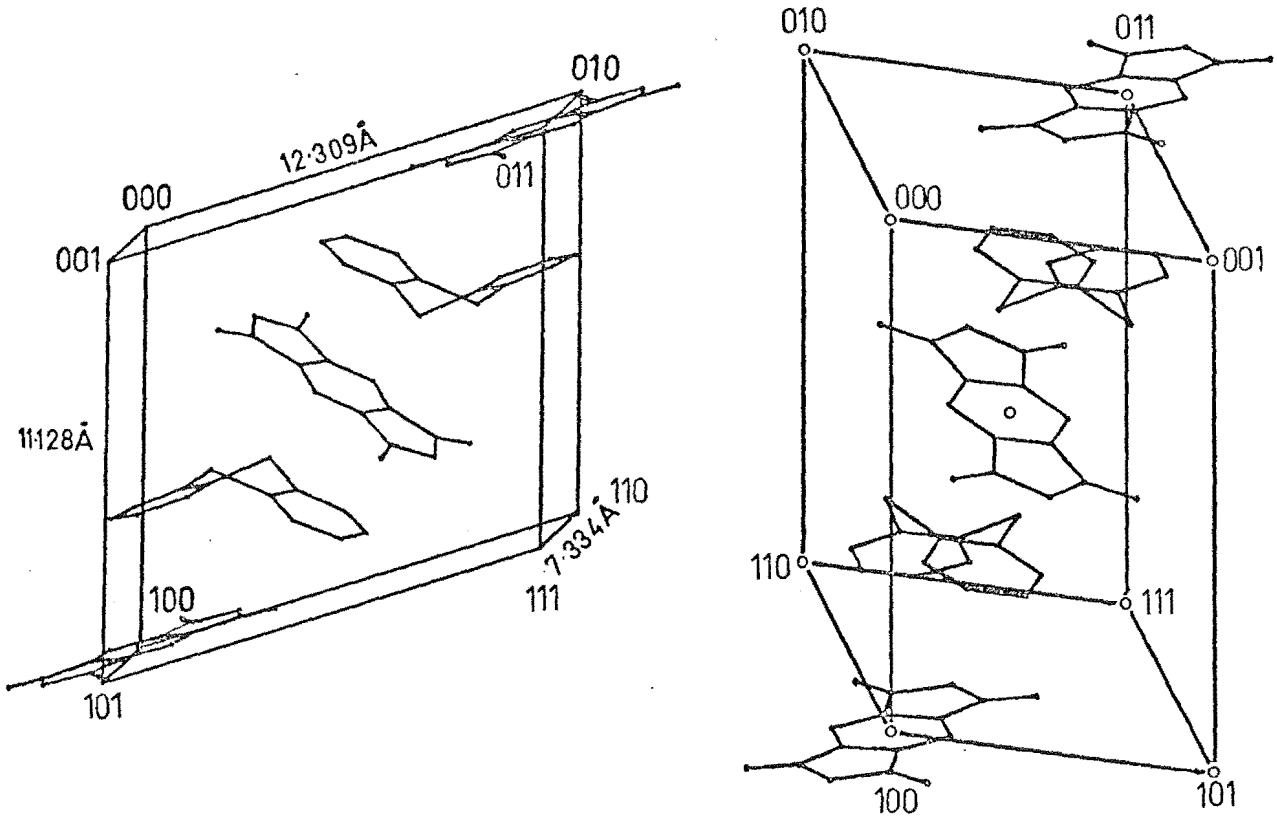


Figure 7.4d

VIEWS OF THE CRYSTAL PACKING OF THIANTHRENE AND PMDA MOLECULES



diagonal may be regarded as the stack axis of the charge-transfer complex. However, as in fluorene PMDA (Evans & Robinson 1980a) there is an alternative view in which the structure is regarded as consisting of thianthrene and PMDA molecules stacked separately parallel to the [001] direction. Atomic parameters are listed in Table 7.4a, root-mean-square amplitudes of vibration in Table 7.4b and structure factors in Appendix A3.

In contrast with other charge-transfer complexes it is interesting to note that with the PMDA molecules lying parallel to the 'wings' of the thianthrene molecule there is no straight path which passes through parallel consecutive molecules in close contact along a stack axis. These features are relevant to any discussion of electron 'hopping' mechanism for electron and exciton motion and photoconductive properties of this type of complex. (Viz. Chapters 2 & 9)

Table 7.4a

ATOMIC PARAMETERS FOR THIANTHRENE PMDA

Atom	x	y	z	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S(1)	0.6382(1)	0.2935(1)	0.0652(2)	0.0136(2)	0.0073(1)	0.0267(4)	0.0047(1)	-0.0049(2)	0.0010(2)
S(2)	0.6022(1)	0.1910(1)	0.4665(2)	0.0106(2)	0.0084(1)	0.0283(4)	0.0017(1)	0.0027(2)	0.0039(2)
C(41)	0.7250(4)	0.3723(4)	0.2530(7)	0.0091(5)	0.0062(4)	0.025(1)	0.0038(4)	-0.003(6)	0.0008(5)
C(42)	0.8086(5)	0.4805(4)	0.2357(8)	0.0107(5)	0.0064(4)	0.030(1)	0.0031(4)	0.0011(7)	0.0026(6)
C(43)	0.8706(5)	0.5432(4)	0.383(1)	0.0084(5)	0.0069(4)	0.045(2)	0.0030(4)	-0.0006(8)	-0.0004(8)
C(44)	0.8548(5)	0.5004(5)	0.5487(9)	0.0085(5)	0.0101(5)	0.034(2)	0.0043(4)	-0.0036(7)	-0.0047(8)
C(46)	0.7092(4)	0.3275(4)	0.4190(7)	0.0085(5)	0.0070(4)	0.026(1)	0.0034(4)	0.0005(6)	-0.0003(6)
C(31)	0.6542(4)	0.1543(4)	0.0701(8)	0.0088(5)	0.0068(4)	0.030(1)	0.0029(4)	-0.0051(7)	-0.0009(6)
C(32)	0.6798(5)	0.0901(5)	-0.0946(8)	0.0137(7)	0.0089(5)	0.029(1)	0.0042(5)	-0.0066(8)	-0.0026(7)
C(33)	0.6844(6)	-0.0209(5)	-0.094(1)	0.0127(7)	0.0079(5)	0.041(2)	0.0040(5)	-0.0083(9)	-0.0042(8)
C(34)	0.6683(5)	-0.0648(4)	0.070(1)	0.0107(6)	0.0057(4)	0.055(2)	0.0028(4)	-0.008(1)	-0.0016(9)
C(35)	0.6467(5)	-0.0004(4)	0.2354(9)	0.0095(5)	0.0071(5)	0.039(2)	0.0013(4)	-0.0030(8)	0.0047(7)
C(36)	0.6381(4)	0.1107(4)	0.2360(8)	0.0074(5)	0.0060(4)	0.032(1)	0.0013(3)	-0.0032(6)	0.0018(6)
C(11)	1.0242(5)	0.0559(4)	-0.1660(7)	0.0097(5)	0.0097(5)	0.024(1)	0.0029(4)	0.0003(6)	0.0031(6)
C(13)	0.9777(4)	0.0582(4)	0.1659(7)	0.0085(5)	0.0072(4)	0.022(1)	0.0027(4)	-0.0022(6)	-0.0002(6)
C(14)	0.9930(5)	0.2300(5)	0.0622(9)	0.0100(6)	0.0072(5)	0.038(2)	0.0022(4)	0.0008(8)	0.0017(8)
C(15)	0.9556(5)	0.1425(5)	0.3257(9)	0.0108(6)	0.0124(6)	0.029(2)	0.0047(5)	-0.0048(8)	-0.0016(8)
C(21)	0.4806(5)	0.4473(4)	0.6692(7)	0.0102(5)	0.0071(4)	0.022(1)	0.0035(4)	0.0002(6)	0.0006(6)
C(22)	0.4149(4)	0.3978(4)	0.5185(7)	0.0076(4)	0.0058(4)	0.026(1)	0.0028(3)	0.0006(6)	0.0011(6)
C(23)	0.4329(4)	0.4478(4)	0.3538(7)	0.0078(4)	0.0064(4)	0.024(1)	0.0029(3)	0.0001(6)	-0.0004(5)
C(24)	0.3126(5)	0.2872(4)	0.4903(8)	0.0101(6)	0.0071(5)	0.031(2)	0.0035(4)	0.007(8)	0.0003(7)
C(25)	0.3439(5)	0.3698(5)	0.2239(8)	0.0100(6)	0.0095(5)	0.027(1)	0.0047(4)	-0.0024(7)	-0.0032(7)
O(11)	1.0051(5)	0.3048(3)	-0.0249(8)	0.0198(6)	0.0081(4)	0.060(2)	0.0045(4)	0.0031(8)	0.0089(7)
O(12)	0.9668(4)	0.2440(3)	0.2549(6)	0.0130(5)	0.0086(3)	0.037(1)	0.0038(3)	-0.0043(6)	-0.0033(5)
O(13)	0.9326(5)	0.1351(5)	0.4857(6)	0.0241(7)	0.0207(6)	0.021(1)	0.0119(5)	-0.0033(7)	-0.0021(6)
O(21)	0.2670(4)	0.2154(3)	0.5914(7)	0.0142(5)	0.0077(3)	0.048(1)	0.0015(3)	0.0021(7)	0.0062(6)
O(22)	0.2753(4)	0.2746(3)	0.3116(5)	0.0108(4)	0.0072(3)	0.033(1)	0.0022(3)	-0.0016(5)	-0.0024(5)
O(23)	0.3270(4)	0.3771(4)	0.0700(6)	0.0146(5)	0.0156(5)	0.025(1)	0.0048(4)	-0.0051(6)	-0.0017(6)
H(111)	1.0427	0.0816	-0.2711	6.0					
H(112)	1.0022	-0.0207	-0.2616	6.0					
H(211)	0.4112	0.4331	0.4117	6.0					
H(212)	0.4700	0.4210	0.7614	6.0					
H(42)	0.8185	0.5065	0.0959	6.0					
H(43)	0.9203	0.6235	0.3784	6.0					
H(44)	0.8978	0.5457	0.6539	6.0					
H(45)	0.7620	0.3550	0.6756	6.0					
H(32)	0.6893	0.1234	-0.2047	6.0					
H(33)	0.7001	-0.0636	-0.2137	6.0					
H(34)	0.6795	-0.1395	0.0702	6.0					
H(35)	0.6416	-0.0277	0.3520	6.0					

Thermal parameters are in the form of $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})]$

Table 7.4b

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION FOR THIANTHRENE PMDA (Å)

	Min	Int	Max
S(1)	0.200(2)	0.246(2)	0.296(2)
S(2)	0.213(2)	0.255(2)	0.295(2)
C(41)	0.177(7)	0.237(6)	0.261(7)
C(42)	0.201(7)	0.239(6)	0.289(7)
C(43)	0.200(7)	0.226(7)	0.352(8)
C(44)	0.200(7)	0.228(7)	0.341(8)
C(45)	0.211(7)	0.251(7)	0.290(7)
C(46)	0.186(6)	0.232(6)	0.274(7)
C(31)	0.204(7)	0.210(7)	0.295(7)
C(32)	0.222(7)	0.249(8)	0.319(7)
C(33)	0.212(7)	0.242(8)	0.360(8)
C(34)	0.192(8)	0.230(8)	0.390(8)
C(35)	0.211(7)	0.238(7)	0.323(7)
C(36)	0.196(7)	0.212(7)	0.290(6)
C(11)	0.228(6)	0.250(7)	0.263(7)
C(12)	0.209(6)	0.224(7)	0.260(6)
C(13)	0.211(6)	0.215(7)	0.252(7)
C(14)	0.221(7)	0.237(6)	0.323(8)
C(15)	0.227(8)	0.255(7)	0.321(8)
C(21)	0.202(6)	0.242(6)	0.256(7)
C(22)	0.181(6)	0.214(6)	0.266(7)
C(23)	0.183(6)	0.220(6)	0.262(7)
C(24)	0.202(7)	0.243(7)	0.298(8)
C(25)	0.200(7)	0.238(7)	0.308(7)
O(11)	0.211(6)	0.326(5)	0.412(6)
O(12)	0.222(5)	0.265(5)	0.338(5)
O(13)	0.229(6)	0.309(6)	0.413(6)
O(21)	0.214(5)	0.293(5)	0.364(5)
O(22)	0.208(5)	0.249(5)	0.316(5)
O(23)	0.238(5)	0.288(5)	0.344(5)
O(23)	0.238(5)	0.288(5)	0.344(5)

CHAPTER 8

THE CHARGE-TRANSFER COMPLEX BIPHENYL TRINITROFLUORENONE

8.1 INTRODUCTION

Biphenyl trinitrofluorenone (B-TNF) is a charge-transfer complex in which biphenyl as in the complex biphenyl tetracyanobenzene (Mohwald & Sackmann 1973), acts as the donor and trinitrofluorenone as the acceptor. This accords with the behaviour of trinitrofluorenone in the complex trinitrofluorenone hexamethylbenzene, as described by Brown, Cheung, Trefonas and Majeste (1974).

8.2 EXPERIMENTAL SECTION

Crystals were kindly supplied by D. Haarer. They are yellow in colour and had been grown by the Bridgman method from zone refined biphenyl and trinitrofluorenone (Haarer 1974). Systematic absences h0l l odd, 0k0 k odd uniquely indicate the space group $P2_1/c$. The density of the crystal was measured by flotation D_m = 1.42g cm^{-3}. Least-squares refinement of the cell constants (using 12 centred reflections) as $\underline{a}$ = 7.195(1), $\underline{b}$ = 28.108(9), $\underline{c}$ = 21.065(7) Å; β = 94.26(2)° yields a calculated density of 1.47 g cm^{-3} with eight molecular pairs in the unit cell.

Cu K_α X-radiation (λ = 1.5418 Å) was used. Data were collected for one quadrant of reciprocal space with $\theta < 57°$, with an Hilger and Watts automatic diffractometer. The intensities of the diffracted X-rays were measured with a 72 step 0.01° scan with 18 second background counts at each end of the scan. Attenuators were used when the monitored pulses exceeded 8000/second. The intensities of 3 standard reflections were monitored every 50 reflections, and the data scaled accordingly. Lorentz and polarisation corrections were applied and, of the unique reflections measured 3247 had intensities > 3σ. Absorption corrections were made and the maximum and minimum values were 1.55 and 1.171 respectively. The linear absorption coefficient is

$9.35cm^{-1}$. Following this, further scaling, based on the equivalence of hk0 and $\bar{h}k0$ reflections were carried out. A linear variation in scale factor, was assumed for the hkl reflection intensities, between successive hk0 and h k+1 0 reflections. (See Appendix B.) In this case such additional scale factors were applied to partially offset the effects of detectable crystal movements.

8.3 STRUCTURE DETERMINATION AND REFINEMENT

Fifty-eight of the seventy non-hydrogen atoms were located by use of the direct methods program MULTAN (Main, Woolfson & Germain 1971) utilizing the 249 reflections having E > 2.0. The twelve remaining atoms were located using conventional difference Fourier techniques. Refinement, in blocks with isotropic thermal parameters for the atoms resulted in a value for R_1 of 0.148.

Refinement of the 630 parameters required by a seventy atom model (anisotropic thermal parameters) is very expensive. It necessitates varying blocks of the parameters rather than the model as a whole. The blocks used were those for whole molecules or pairs of molecules. Program BONDSTAT was used to obtain comparative estimates, of standard deviations, of equivalent sets of bonds between molecules, to help determine the order of refinement of blocks. The entire model was not refined to convergence because of the cost involved, but to a point where $R_1 = 0.108$. When comparison is made with the similar structure analyses reported in this thesis, the expected minimum value of R_1 is approximately 0.075. It is felt that with R_1 at 0.108 this is a satisfactory state in which to leave this structure.

8.4 DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of the complex consists of alternately positioned biphenyl and trinitrofluorenone molecules. Figures 8.4a, 8,4b, 8.4c, and 8.4d define the atom labelling scheme used. Figure 8.4e shows the spatial relationships within the unit cell.

Figure 8.4a

DISTANCES AND ANGLES IN BIPHENYL (1)

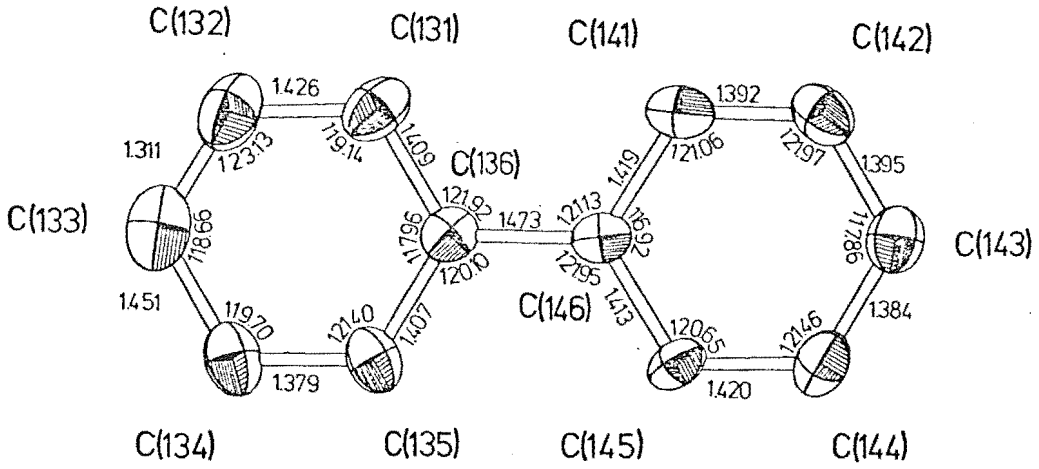


Figure 8.4b

DISTANCES AND ANGLES IN BIPHENYL (2)

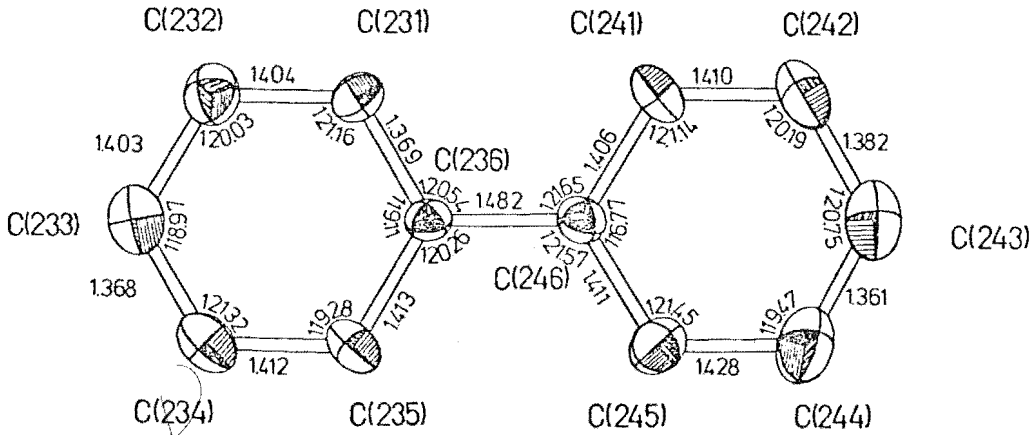


Figure 8.4c

DISTANCES AND ANGLES IN TNF (1)

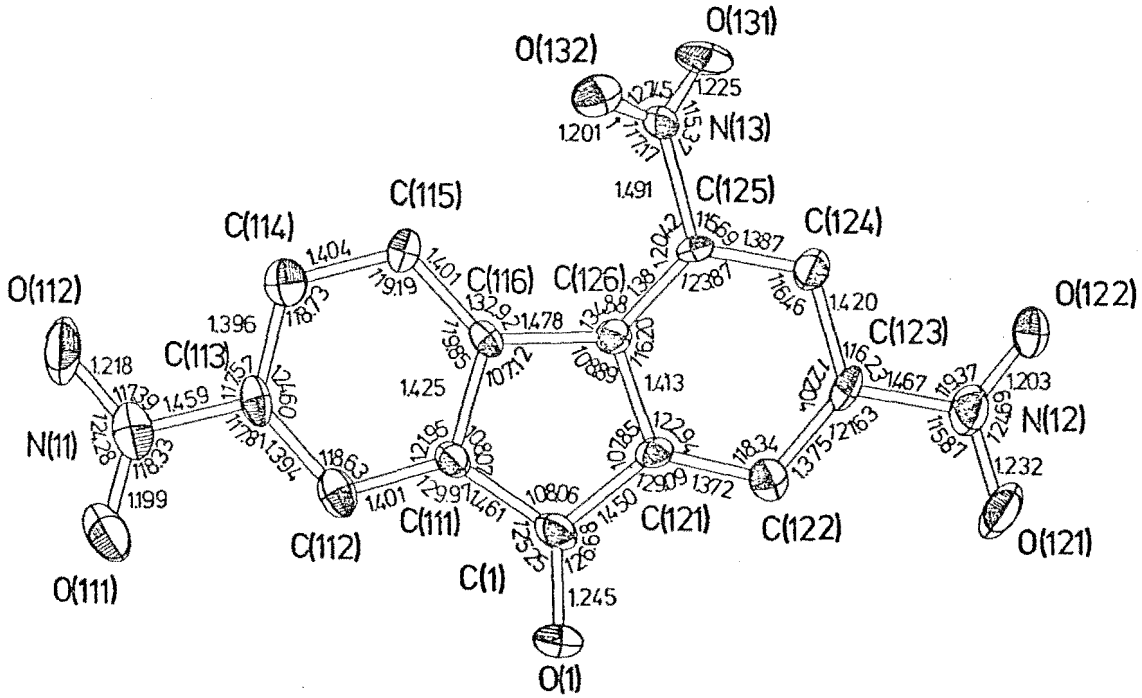


Figure 8.4d

DISTANCES AND ANGLES IN TNF (2)

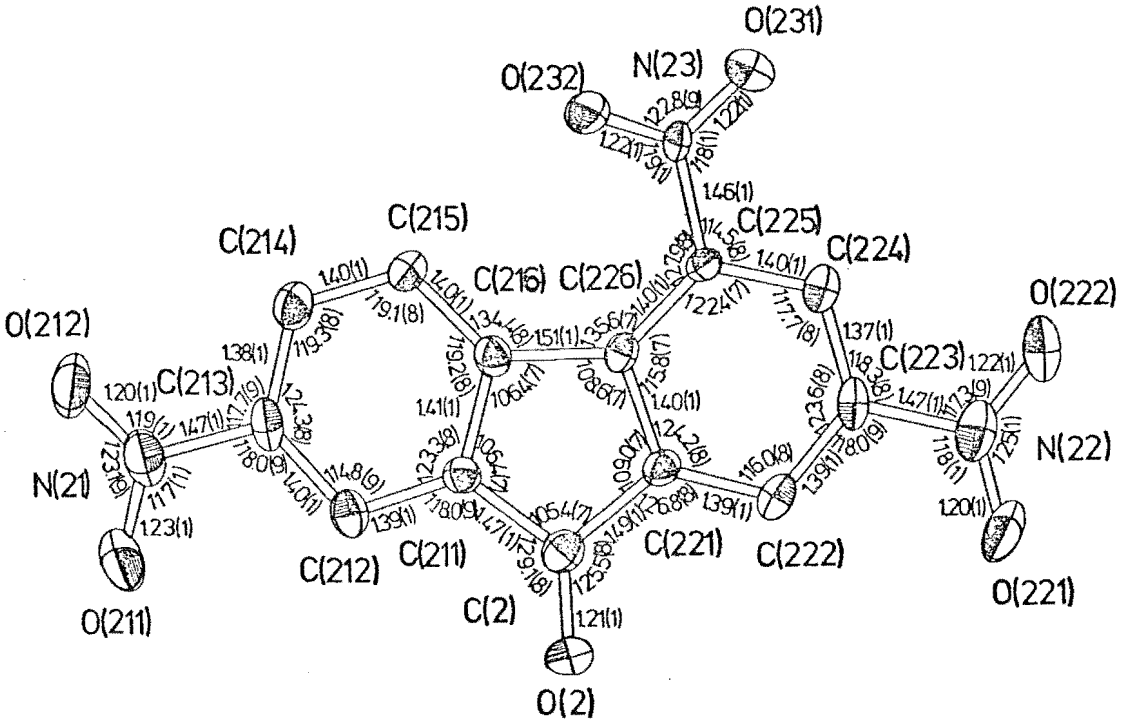
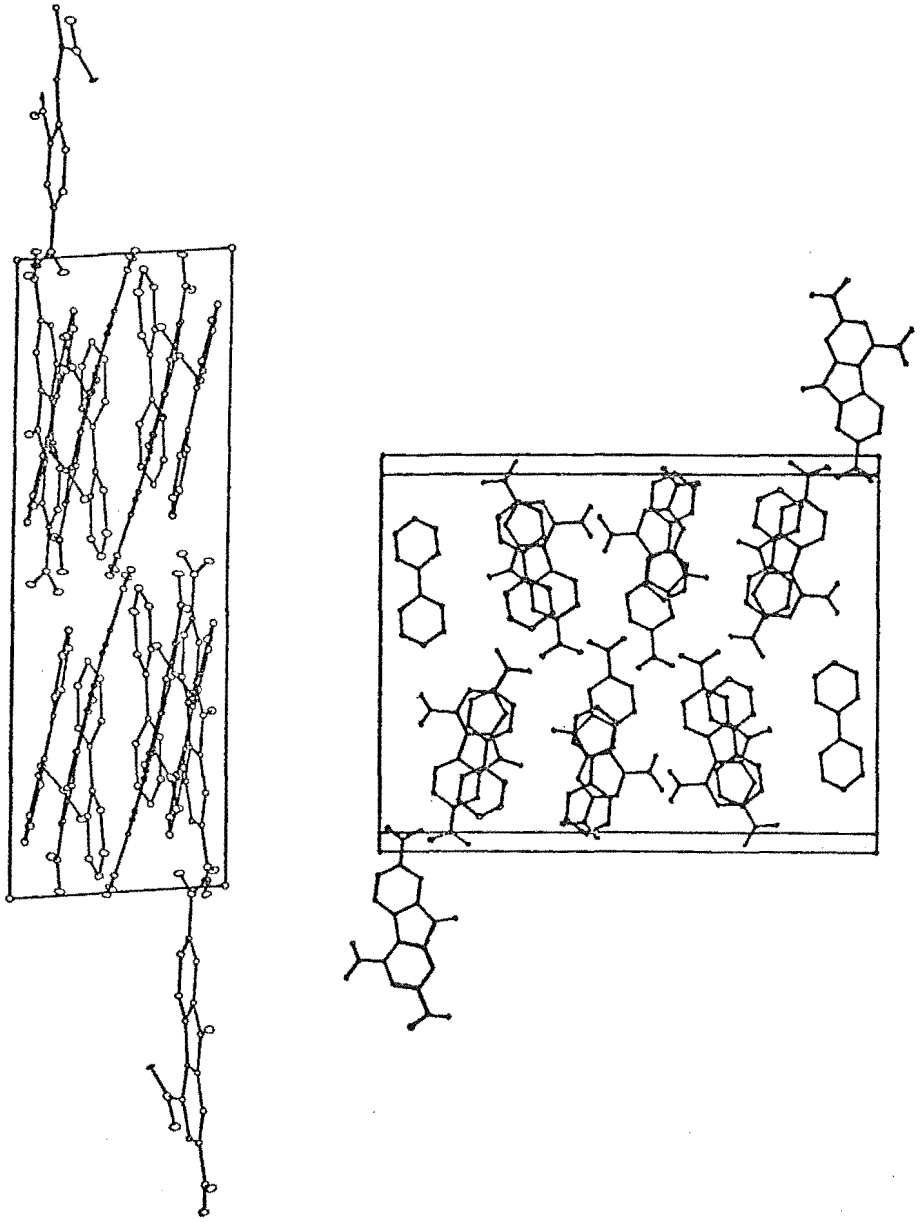


Figure 8.4e

VIEWS OF THE CRYSTAL PACKING OF BIPHENYL AND TRINITROFLUORENONE



It is unusual to have two molecular pairs in the same asymmetric unit. It does, however, give an opportunity to obtain a measure of variation of the geometry of molecules in the crystalline state. Consider the biphenyl molecules. Let their molecular planes be denoted by B and their phenyl rings by a and b. Table 8.4a contains interplanar angles for the biphenyl molecules. Reference to Figures 8.4a and 8.4b indicates that the deviation from planarity is principally a twist about the axial direction defined by the bond C(36) - C(46). The a and b planes are folded towards each other slightly and this accounts for the unequal sizes of the angles a1 - B1, b1 - B1 and a2 - B2, b2 - B2.

The axial twist is in contrast to that observed for biphenyl in the crystalline state (Trotter 1961), whereas it is in accord with the situation prevailing in the vapour phase (Karle & Brockway 1944).

Table 8.4a

INTERPLANAR ANGLES WITHIN BIPHENYL MOLECULES

	Biphenyl 1	Biphenyl 2
	Interplanar Angles (°)	
Planes		
a - b	6.99	8.33
a - B	3.44	4.15
b - B	3.55	4.18

For the trinitrofluorenone molecules denote the molecular planes as TNF, the molecular plane devoid of the $-NO_2$ groups TF and the planes of the NO_2 groups as cN, dN, and eN. Table 8.4b contains the interplanar angles for the trinitrofluorenone molecules.

Table 8.4b

INTERPLANAR ANGLES FOR TRINITROFLUORENONE MOLECULES

Planes	TNF 1	TNF 2	
	Interplanar angles (°)		
TF - TNF	1.66	2.63	
TF - cN	17.77	12.69	
TF - dN	127.62	156.13	
TF - eN	4.33	174.11	= -5.89
TNF cN	18.50	10.06	
TNF - dN	128.16	156.30	
TNF - eN	4.52	171.90	= -8.10

The orientations of the $-NO_2$ groups show considerable variation as can be seen in figure 8.4e. Table 8.4c contains angles between biphenyl and trinitrofluorenone planes within each molecular pair.

Table 8.4c

INTERPLANAR ANGLES WITHIN B AND TNF PAIRS

Planes	B-TNF 1	B-TNF 2
	Interplanar Angles (°)	
a - TNF	4.71	3.72
a - TF	3.31	6.34
b - TNF	4.41	4.72
b - TF	5.56	2.62
B - TNF	2.82	0.83
B - TF	2.82	2.49

The angle between normals to the two biphenyl molecules is 21.28°, between TF1 and TF2 20.94° and between the trinitrofluorenone molecules 23.45°. Table 8.4b shows that the greatest differences occurring in the molecular geometry are the differences in orientation of the three $-NO_2$ groups, these being

of the order of five, thirty and ten degrees for the c, d and e planes respectively. These variations are probably due to crystal packing effects,rather than determining them, as losses in 'conjugation energy' from nitro-group rotations are small (0.6 kcal/mole - Dashevskii, Struchkov & Akopyan 1966). The average perpendicular distance between biphenyl and trinitrofluorenone molecules is 3.36 Å whereas the distance between them along the stack axis is 3.598 Å.

In certain analyses involving trinitrofluorenone a shortening of the C(1)-C(111), C(2)-C(211) bond lengths relative to the equivalent bond lengths C(1)-C(121), C(2)-C(221) has been observed (Brown et al. 1974). In this analysis small shortenings of 0.04 and 0.02 Å respectively in the two molecules are observed. The long bonds C(116)-C(126), C(216)-C(226) are 1.51 Å in accord with the corresponding bond length in the fluorene molecule of fluorene PMDA.

Atomic parameters are listed in Table 8.4d and structure factors in Appendix A4. Root-mean-square amplitudes of vibration for trinitrofluorenone (2) are given in Table 8.4e. Values were not calculated for the other molecules, but are expected to be of similar magnitude.

Table 8.4d

ATOMIC PARAMETERS FOR BIPHENYL TRINITROFLUORENONE

Atom	x	y	z	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(131)	0.133(2)	0.2511(5)	0.3239(7)	0.023(3)	0.0019(2)	0.0031(3)	-0.0023(6)	-0.0003(8)	0.0005(2)
C(132)	0.088(2)	0.2569(6)	0.3878(8)	0.034(4)	0.0026(2)	0.0026(4)	-0.0023(7)	-0.0001(7)	0.0003(2)
C(133)	0.066(2)	0.3014(6)	0.4117(8)	0.019(3)	0.0031(2)	0.0028(4)	-0.0010(7)	0.0001(9)	-0.0001(2)
C(134)	0.086(2)	0.3425(5)	0.3713(7)	0.018(3)	0.0022(2)	0.0025(3)	-0.0007(6)	-0.0004(8)	-0.0006(2)
C(135)	0.130(2)	0.3362(5)	0.3091(6)	0.018(3)	0.0017(2)	0.0025(3)	-0.0000(5)	-0.0004(7)	-0.0005(2)
C(136)	0.154(2)	0.2905(4)	0.2838(6)	0.013(2)	0.0013(2)	0.0022(3)	-0.0004(5)	-0.0007(6)	0.0001(2)
C(141)	0.198(2)	0.2393(5)	0.1880(7)	0.015(3)	0.0011(2)	0.0037(3)	0.0001(5)	0.0007(7)	-0.0000(2)
C(142	0.231(2)	0.2341(5)	0.1241(7)	0.018(3)	0.0015(2)	0.0036(3)	-0.0001(6)	0.0020(8)	-0.0006(2)
C(143)	0.260(2)	0.2731(5)	0.0852(7)	0.021(3)	0.0019(2)	0.0026(3)	-0.0002(6)	0.0012(8)	0.0000(2)
C(144)	0.261(2)	0.3179(5)	0.1125(7)	0.026(3)	0.0018(2)	0.0024(3)	0.0004(5)	0.0015(7)	0.0005(2)
C(145)	0.230(2)	0.3243(5)	0.1778(6)	0.019(3)	0.0011(1)	0.0025(3)	0.0005(5)	0.0011(7)	0.0006(2)
C(146)	0.194(2)	0.2845(4)	0.2166(6)	0.009(2)	0.0011(1)	0.0026(2)	-0.0000(4)	-0.0003(6)	0.0001(2)
C(231)	0.308(2)	0.0337(5)	0.2392(7)	0.016(2)	0.0009(1)	0.0021(2)	0.0003(4)	0.0006(6)	-0.0002(2)
C(232)	0.304(2)	0.0286(5)	0.1728(7)	0.023(3)	0.0014(2)	0.0023(3)	0.0011(5)	0.0007(7)	-0.0001(2)
C(233)	0.351(2)	0.0672(5)	0.1349(7)	0.017(3)	0.0019(2)	0.0023(3)	0.0007(5)	0.0007(7)	0.0001(2)
C(234)	0.412(2)	0.1085(5)	0.1639(6)	0.019(3)	0.0015(5)	0.0025(3)	0.0006(5)	0.0006(6)	0.0006(2)
C(235)	0.419(2)	0.1137(5)	0.2307(6)	0.020(2)	0.0012(1)	0.0021(3)	0.0005(5)	0.0013(6)	0.0006(2)
C(236)	0.364(2)	0.0754(4)	0.2684(5)	0.014(2)	0.0007(1)	0.0017(2)	0.0004(4)	0.0006(5)	0.0000(1)
C(241)	0.355(2)	0.0396(5)	0.3778(6)	0.022(3)	0.0014(1)	0.0019(3)	0.0000(5)	0.0006(6)	0.0007(2)
C(242)	0.364(2)	0.0439(5)	0.4447(7)	0.030(3)	0.0019(2)	0.0022(3)	0.0013(6)	0.0020(7)	0.0007(2)
C(243)	0.412(2)	0.0869(6)	0.4732(8)	0.031(3)	0.0025(2)	0.0024(4)	0.0013(7)	0.0012(9)	-0.0001(2)
C(244)	0.435(2)	0.1266(6)	0.4375(8)	0.037(3)	0.0023(2)	0.0027(4)	0.0003(7)	0.0022(9)	-0.0006(2)
C(245)	0.417(2)	0.1231(5)	0.3696(7)	0.026(3)	0.0013(2)	0.0025(3)	-0.0011(5)	0.0016(7)	-0.0004(2)
C(246)	0.377(2)	0.0793(4)	0.3387(6)	0.017(2)	0.0009(1)	0.0018(2)	0.0005(4)	0.0008(6)	0.0001(1)
C(111)	0.619(2)	0.3017(4)	0.3251(5)	0.015(3)	0.0009(1)	0.0011(3)	-0.0008(5)	0.0003(6)	0.0001(2)
C(112)	0.566(2)	0.3055(4)	0.3877(6)	0.014(3)	0.0015(2)	0.0012(3)	-0.0004(6)	-0.0005(7)	0.0000(2)
C(113)	0.546(2)	0.3517(4)	0.4101(5)	0.014(3)	0.0015(2)	0.0008(3)	-0.0005(5)	0.0001(7)	-0.0003(2)
C(114)	0.578(2)	0.3928(4)	0.3753(6)	0.014(3)	0.0013(2)	0.0017(3)	0.0001(6)	-0.0004(8)	-0.0001(2)
C(115)	0.630(1)	0.3881(4)	0.3127(5)	0.014(3)	0.0009(2)	0.0014(3)	0.0002(5)	0.0003(7)	-0.0003(2)
C(116)	0.653(1)	0.3425(4)	0.2877(5)	0.016(3)	0.0009(2)	0.0008(3)	0.0001(5)	0.0003(6)	0.0002(2)
C(121)	0.692(1)	0.2750(4)	0.2240(5)	0.012(2)	0.0005(1)	0.0014(2)	-0.0009(5)	-0.0002(6)	-0.0000(2)
C(122)	0.717(2)	0.2483(4)	0.1708(5)	0.016(3)	0.0011(2)	0.0015(3)	0.0001(6)	0.0005(7)	0.0000(2)
C(123)	0.758(2)	0.2716(4)	0.1161(5)	0.016(3)	0.0009(2)	0.0015(3)	0.0002(5)	-0.0006(7)	-0.0006(2)
C(124)	0.765(2)	0.3220(4)	0.1125(5)	0.017(3)	0.0009(2)	0.0015(3)	0.0004(5)	0.0004(7)	-0.0001(2)
C(125)	0.741(1)	0.3466(4)	0.1683(5)	0.017(2)	0.0004(1)	0.0017(3)	-0.0001(5)	0.0010(6)	0.0000(2)
C(126)	0.700(2)	0.3252(4)	0.2245(5)	0.016(3)	0.0007(2)	0.0013(3)	-0.0005(5)	-0.0003(6)	-0.0000(2)
C(1)	0.644(2)	0.2594(4)	0.2863(6)	0.020(3)	0.0010(2)	0.0015(3)	0.0005(6)	0.0004(7)	0.0005(2)
O(1)	0.624(1)	0.2176(3)	0.3041(4)	0.028(2)	0.0008(1)	0.0024(2)	-0.0010(4)	0.0016(5)	0.0004(1)
N(11)	0.484(2)	0.3577(4)	0.4740(5)	0.021(3)	0.0019(2)	0.0018(3)	-0.0002(6)	0.0014(8)	-0.0002(2)
O(111)	0.449(1)	0.3228(3)	0.5035(4)	0.032(3)	0.0023(2)	0.0019(3)	-0.0009(5)	0.0022(7)	0.0003(2)
O(112)	0.469(1)	0.3982(4)	0.4936(5)	0.051(3)	0.0024(2)	0.0030(4)	-0.0017(6)	0.0075(8)	-0.0012(2)
N(12)	0.784(1)	0.2457(4)	0.0569(5)	0.024(3)	0.0013(2)	0.0020(3)	-0.0011(6)	0.0007(8)	-0.0006(2)
O(121)	0.812(1)	0.2026(3)	0.0626(4)	0.037(2)	0.0012(2)	0.0028(3)	0.0009(5)	0.0003(7)	-0.0010(2)
O(122)	0.770(1)	0.2667(3)	0.0070(5)	0.054(3)	0.0014(2)	0.0014(3)	-0.0012(5)	0.0019(7)	-0.0005(2)
N(13)	0.759(1)	0.3994(3)	0.1645(5)	0.032(3)	0.0007(2)	0.0015(3)	0.0018(5)	0.0030(7)	0.0004(2)
O(131)	0.672(1)	0.4180(3)	0.1188(5)	0.047(3)	0.0010(2)	0.0026(3)	0.0013(5)	0.0002(7)	0.0010(2)
O(132)	0.858(1)	0.4186(3)	0.2051(4)	0.032(2)	0.0010(1)	0.0027(3)	-0.0013(4)	0.0009(6)	-0.0001(2)
C(211)	0.860(1)	0.4243(3)	0.6813(4)	0.014(2)	0.0008(1)	0.0016(2)	-0.0001(4)	0.0005(5)	-0.0000(1)
C(212)	0.870(1)	0.4175(3)	0.6163(4)	0.017(2)	0.0014(1)	0.0015(3)	-0.0004(5)	-0.0004(6)	-0.0001(2)
C(213)	0.837(1)	0.4584(4)	0.5792(4)	0.021(3)	0.0016(2)	0.0010(2)	-0.0011(5)	0.0006(6)	0.0000(2)
C(214)	0.796(1)	0.5025(3)	0.6033(5)	0.025(3)	0.0012(2)	0.0018(3)	-0.0008(5)	0.0012(7)	0.0002(2)
C(215)	0.790(1)	0.5081(3)	0.6690(4)	0.023(3)	0.0009(1)	0.0017(3)	0.0002(5)	0.0001(6)	0.0002(2)
C(216)	0.822(1)	0.4687(3)	0.7087(4)	0.015(2)	0.0009(1)	0.0015(2)	-0.0006(4)	-0.0001(6)	-0.0001(1)
C(221)	0.879(1)	0.4134(3)	0.7923(4)	0.014(2)	0.0008(1)	0.0017(2)	0.0009(4)	0.0015(6)	0.0002(1)
C(222)	0.906(1)	0.3941(3)	0.8530(4)	0.016(2)	0.0011(1)	0.0018(3)	-0.0003(4)	0.0002(6)	0.0005(2)
C(223)	0.888(1)	0.4256(3)	0.9032(4)	0.018(2)	0.0016(2)	0.0011(2)	-0.0002(5)	-0.0001(6)	0.0002(2)
C(224)	0.842(1)	0.4726(3)	0.8952(4)	0.015(2)	0.0013(1)	0.0016(2)	-0.0000(5)	-0.0001(6)	0.0003(1)
C(225)	0.811(1)	0.4895(3)	0.8329(4)	0.015(2)	0.0007(1)	0.0015(2)	0.0005(4)	0.0009(5)	0.0002(1)
C(226)	0.833(1)	0.4611(3)	0.7797(4)	0.011(2)	0.0009(1)	0.0013(2)	-0.0000(4)	-0.0003(5)	0.0002(1)
C(2)	0.895(1)	0.3880(3)	0.7308(4)	0.016(2)	0.0010(1)	0.0020(3)	-0.0003(5)	0.0003(6)	0.0001(2)
O(2)	0.931(1)	0.3464(2)	0.7251(3)	0.035(2)	0.0009(1)	0.0025(2)	0.0014(4)	0.0007(5)	0.0001(1)
N(21)	0.845(1)	0.4540(4)	0.5100(4)	0.031(3)	0.0017(2)	0.0017(3)	-0.0021(5)	0.0012(6)	-0.0002(2)
O(211)	0.914(1)	0.4174(3)	0.4899(3)	0.045(3)	0.0024(2)	0.0020(2)	-0.0002(5)	0.0028(6)	-0.0003(2)
O(212)	0.787(1)	0.4856(3)	0.4761(3)	0.054(3)	0.0020(1)	0.0017(2)	-0.0021(5)	-0.0005(6)	0.0004(1)
N(22)	0.919(1)	0.4070(4)	0.9686(4)	0.023(2)	0.0021(2)	0.0020(3)	0.0004(5)	-0.0009(6)	0.0006(2)
O(221)	0.949(1)	0.3651(3)	0.9751(3)	0.049(3)	0.0019(1)	0.0023(2)	0.0002(5)	-0.0012(6)	0.0010(1)
O(222)	0.914(1)	0.4354(3)	1.0120(3)	0.046(3)	0.0026(2)	0.0015(2)	0.0007(5)	0.0000(6)	0.0002(1)
N(23)	0.747(1)	0.5389(3)	0.8282(5)	0.023(3)	0.0010(2)	0.0009(3)	0.0012(5)	-0.0006(8)	0.0002(2)
O(231)	0.776(1)	0.5642(2)	0.8750(3)	0.060(3)	0.0012(1)	0.0024(2)	0.0021(4)	0.0003(6)	-0.0004(1)
O(232)	0.6604(9)	0.5526(2)	0.7794(3)	0.040(2)	0.0012(1)	0.0020(1)	0.0024(3)	-0.0027(4)	-0.0001(1)

Thermal parameters are in the form of $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})]$

Table 8.4e

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION OF TRINITROFLUORENONE (2) (Å)

C(211)	0.18(1)	0.19(1)	0.20(1)
C(212)	0.17(1)	0.21(1)	0.24(1)
C(213)	0.15(1)	0.21(1)	0.27(1)
C(214)	0.18(1)	0.23(1)	0.26(1)
C(215)	0.17(1)	0.21(1)	0.25(1)
C(216)	0.17(2)	0.19(1)	0.21(1)
C(221)	0.16(1)	0.17(1)	0.23(1)
C(222)	0.17(2)	0.20(1)	0.24(1)
C(223)	0.15(2)	0.22(1)	0.26(1)
C(224)	0.17(1)	0.20(1)	0.23(1)
C(225)	0.16(1)	0.17(1)	0.21(1)
C(226)	0.15(2)	0.18(1)	0.20(1)
C(2)	0.19(1)	0.20(1)	0.22(1)
O(2)	0.18(1)	0.238(9)	0.308(9)
N(21)	0.19(1)	0.23(1)	0.31(1)
O(211)	0.20(1)	0.31(1)	0.34(1)
O(212)	0.19(1)	0.27(1)	0.39(1)
N(22)	0.19(1)	0.26(1)	0.30(1)
O(221)	0.18(1)	0.31(1)	0.36(1)
O(222)	0.18(1)	0.32(1)	0.35(1)
N(23)	0.13(1)	0.20(1)	0.26(1)
O(231)	0.19(1)	0.25(1)	0.40(1)
O(232)	0.180(8)	0.210(8)	0.354(8)

CHAPTER 9

REVIEW OF THE CHARGE-TRANSFER STRUCTURES DETERMINED

9.1 STRUCTURE GEOMETRY AND SYMMETRY

The structures studied do show commonly occurring features for this class of compound. For simplicity the order of comparison used shall be that of the thesis chapters. All except thianthrene PMDA have well defined stack axes. The donor-acceptor perpendicular distances are 3.36, 4.46, 3.51 and 3.36 $\mathring{A}$. The distance for fluorene PMDA is unusually long, however its donor-donor and acceptor-acceptor distances are 3.52 $\mathring{A}$. The angles between normals to the molecular planes in the D-A pairs are 4.11°, 9.84°, 4.72°, and 2.82° and 2.49°. Both PMDA and biphenyl molecules can be centrosymmetric. PMDA molecules are found about centres of inversion; (0,0,0) in the fluorene compound, and on two such centres (crystallographically independent), (0,0,0) and (1/2,1/2,1/2) in the thianthrene compound. None of phenanthrene, fluorene, thianthrene and trinitrofluorenone molecules have a centre of inversion, although fluorene is statistically disordered, in the unit cell of the compound. It is interesting that for thianthrene PMDA the situation is mixed. There are two crystallographically dependent molecules about centres of inversion along with two thianthrene molecules (which could have had some mirror plane symmetry) related to each other by the space group centre of inversion. In contrast, in biphenyl trinitro-fluorenone, there are two complete pairs of crystallographically independent molecules in the asymmetric unit. Thianthrene PMDA could be regarded in this way also, if only half molecules were considered. That is two half (connected) PMDA molecules and two half (unconnected) thianthrene molecules.

In biphenyl trinitrofluorenone the two systems run along the same stack axis making similar angles of tilt to it, but tilted with respect to each other, normals to molecular planes making an angle of ~ 21° to each other.

9.2 INTERMOLECULAR CHARGE TRANSFER

This may take place between independent molecules of the same type within the same chemical unit or between molecules of different types. So intermolecular charge transfer is possible in each of these structures betweeen the two types of molecule present in each case. In addition for thianthrene it is also allowed between the independent PMDA molecules, and for biphenyl TNF it is allowed between like members of the crystallographically independent molecular pairs. Fluorene PMDA is likely to have reduced D-A charge transfer due to the large D-A distance giving reduced π-π orbital overlap. However fluorene-fluorene charge transfer should be possible due to the random disordering of the fluorene molecules breaking the cell to cell space group equivalence.

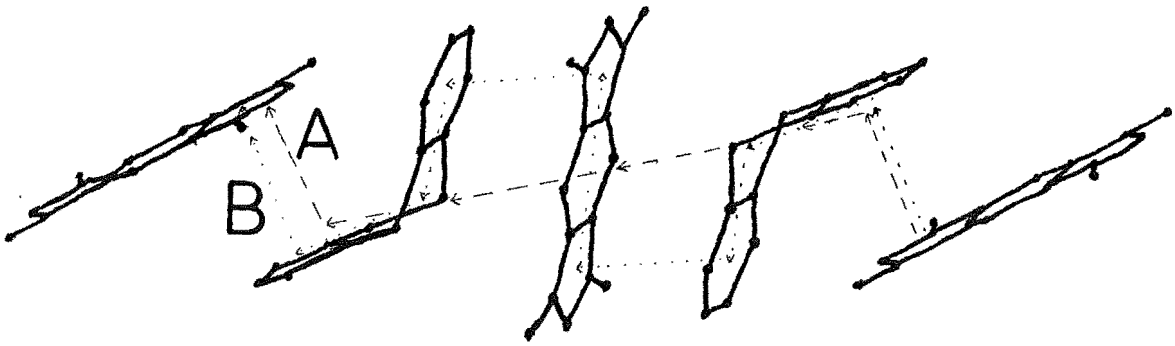
9.3 DIMENSIONALITY OF CHARGE CARRIER MOTION

In a structure such as phenanthrene PMDA maximum charge transfer could be expected where the D-A orbital overlap is greatest, that is, along the stack axis. It could also be expected, to a reduced extent, between D and A molecules on nearest neighbour stacks and on more distant stacks. Hence a large anisotropy could be expected between measurements parallel and perpendicular to the stack axis, whilst between those perpendicular to the stack axis there would be a small anisotropy governed by variations in the donor-acceptor inter-stack distances. That this is the case has been shown by Mohwald & Haarer (1976), the anisotropy of the photocurrents parallel and perpendicular to the stack axis being in the ratio of ~ 20:1. As already discussed, a hopping model (p14) on a quasi 1-D lattice (p12) is an appropriate description. The electron mobility in fluorene PMDA, with its distinctive structure, could be expected to be significaltly different in magnitude and degree of anisotropy, but still predominantly pseudo one-dimensional. Biphenyl is a fairly typical CT complex and so, as far as mechanisms for charge transfer are concerned, could be expected

to behave similarly to phenanthrene PMDA. Thianthrene PMDA has the $\pi - \pi$ overlap for charge transfer but the bent nature of thianthrene may impede easy flow conduction along a specific direction. Several simple-minded models, in which electrons move from molecule to molecule, can be envisaged. They involve hopping from D-A followed by translation within the second molecule. This is illustrated by the pathways shown in Figure 9.3.

Figure 9.3

HOPPING PATHWAYS WITHIN THIANTHRENE PMDA



The pathway of type A utilises hops between central, sulphur containing thianthrene rings, through a central PMDA phenyl ring, a translation between a thianthrene central and end ring, and an end to end PMDA translation. Pathway type B involves end to end PMDA and thianthrene translations, and end ring - thianthrene PMDA hops. If both of these pathways are feasible then others between these two extremes may be possible. Also other routes are possible involving longer hops. The effect of imposing an electric field is generally to assist electron motion in the direction of the electric field. The different effects of electric fields on intermolecular and intramolecular charge transfer, will alter the anisotropy of the measured mobility, in ways which depend on the alignment of the electric field. If the effective resistance and dimensionality of a material can be

altered markedly by a transverse electric field, then it may have useful properties for utilisation in components of electronic devices.

The different hopping distances could give rise to steps in the field dependence of the electron mobility in the directions in which they are found. This would be equivalent to describing the behaviour by a model containing a number of traps. That is to say, some of the traps postulated in the literature may really be manifestations of internal periodicities of the molecular structures comprising the crystalline material.

9.4 SOLID STATE SIGNAL PROCESSING TECHNOLOGIES

The major such technology is that of electronics. Initial developments were based on macroscopic properties of conduction, resistance, capacitance and inductance using centimetre sized components. The advent of the transistor, utilising microscopic crystal defects in 'solid state' components, revolutionised electronics. The subsequent miniaturisation of integrated circuits has achieved a high level of refinement. Micro-processors containing thousands of components, to perform numerous logical functions, are produced on very small silicon chips. In this process of refinement the basic functions of the various components has remained unaltered. The study of new materials and their properties has in some senses advanced ahead of this technology. New materials are being used but a number of their properties are only being superficially utilised. Most solid state technology is based on electronics, and as its name implies, electron motion and its management - storage, resistance, oscillation and direction. Optical and acoustical signals as input or output are transformed to electrical motion very early or late in the sequence of processing. However photons and phonons propagate well in the solid state, and can also be managed, stored and transformed. Optical technologies are being developed, utilising thin film light conduction, diffraction, and excitation of electrons giving photons of

different frequency. The laser is the most popular example of this technology. The optical 'pumping' used therein is in effect a frequency transformation with a simultaneous phase tune. Thin film optical guided waves have considerable potential for use in optical integrated circuitry. Components for such circuitry may be either passive - lenses, prisms, or active - piezoelectric, electro-optic (Garwin 1975).

Where there is an interface between optical and electronic circuitry there is a need for a photoconducting material to transform the optical signal to an electronic one. This makes the study of the structural and physical properties of such materials an important exercise. An increase in understanding of their properties and hierarchical structures will enable development of devices using the microscopic features to much greater advantage than at present. That is to say, on the one hand there are many known discrete energy levels, and on the other hand there are many devices requiring discrete signals of specific magnitude but at the moment only very simple discrete values are used. Such an example is that of computer storage, where a binary system is used corresponding to the two states of a magnetic dipole.

9.5 DYNAMIC ELECTRONICS

Up until recently the great majority of components used in electronic circuitry have individually had a fixed function such as resistance, inductance, capacitance, conduction/non-conduction. Circuitry using such components could be termed Static Electronics. A new field which could be called Dynamic Electronics, in which the function of individual components may vary through a number of modes in sequence, is beginning to open up. A component would be able to have a variable function, that is, to act like a resistor, or capacitor, transistor or other static type component on different occasions. The mode of operation would become programmable. Transistors act like valves, differentiating between current flows in opposite directions. A transistor whose direction of influence

could be altered would be useful. This is normally arranged for by doping (introducing defects) one end of the transistor material in order to make it an electron acceptor. CT complexes can have defects introduced by bending/doping, and excitons produced in them by optical irradiation. Mechanical strains and vibrations can modify the effect of the dopant or dislocation type defect. A pair of such crystal complexes in concert could exhibit differential electrical properties similar to a conventional transistor, but be able to have their characteristics dynamically modified. Two techniques for modification are application of electric fields, and imposition of strains using piezo-electric crystals, causing changes in the crystal's polarisation and dislocation density respectively. Phosphorescence is modified by the dislocation density, so vibrations in that density would yield a pulsing phosphorescence. Phosphorescence is a time delayed photonic emission. Variation of the delay would give a form of time modulation of the signal input.

9.6 FUTURE SIGNAL PROCESSING TECHNOLOGY

The interface between input acoustical or optical signal and electronics may disappear. In the case of light metering devices the present photon - current circuitry - meter display could be replaced by photon - integrated optics circuitry - visual display. In more complex systems the processor may have input to waveform circuitry followed by dynamic/static electronics. The possible combinations are numerous, and techniques of electron and photon management seem set to become much more sophisticated.

The study of new materials and their characterising properties will, along with their integrated use, yield a new amalgam of interesting phototronics, dynamic and static electronics. Miniaturisation of such systems incorporating organic compounds such as CT complexes for information data processing, will give processors, closer in type to those obviously present, yet only partially understood in the biological world.

CHAPTER 10

THE STRUCTURE OF THE TRIDENTATE, FIVE COORDINATE N-(2-HYDROXYPHENYL) SALICYLALDIMINE DIMETHYL TIN(IV)

10.1 INTRODUCTION

Among the organo-tin compounds pentacoordination is not common. Examples include a number of bridged and polymeric structures where the ligands are functioning as bidentates (Ho & Zuckerman, 1973). However in all mononuclear structures so far reported the ligands are monodentate. In N-(2-hydroxyphenyl) salicylaldimine dimethyl tin(IV) the ligand is potentially tridentate and the structure therefore of considerable interest. The compound was prepared by Ruddick (1973) in the course of investigations of various Schiff base complexes.

10.2 EXPERIMENTAL SECTION

Well formed crystals of $(CH_3)_2Sn(C_6H_4O)CHN(OC_6H_4)$ obtained by recrystallisation from methanol were kindly supplied by Dr. J.R. Sams, University of British Columbia.

Diffraction symmetry mmm and systematic absences of X-ray reflections hk0 for h+k odd, 0kl for k odd, and h0l for l odd, established the space group uniquely as Pbcn. The crystal density was measured by a flotation method using a mixture of bromobenzene and 1,2,-dibromomethane. Least-squares refinement of the cell contents (using 12 centred reflections) as $\underline{a}$ = 19.304(5), $\underline{b}$ = 10.534(3), $\underline{c}$ = 13.398(4) Å yields a calculated density of 1.82g cm^{-3} with 8 molecules in the unit cell.

Zr filtered Mo radiation (λ = 0.7107 Å) was used. Data were collected from the equivalent sets of reflections hkl and $hk\bar{l}$ in that portion of reciprocal space for which $\theta<20^{\circ}$ using an Hilger and Watts automatic diffractometer. The intensities of the diffracted X-rays were measured using an 80 step single second, 0.01° scan with 20 sec. background counts at each end of the scan. Attenuators were used when the monitored pulses exceeded 8000/s, the attenuating factors being 3.16 and 8.28. The intensities of 3

standard reflections were monitored every 100 reflections and the data scaled accordingly. Lorentz and polarisation corrections were applied and, of the unique reflections measured 1024 had intensities $>\sigma$. Absorption corrections (by Gaussian integration) were applied, and the two equivalent data sets averaged.

10.3 STRUCTURE SOLUTION AND REFINEMENT

All non-hydrogen atoms were located by the application of conventional heavy-atom procedures using the Sn atom, located from the Patterson function, for initial phasing. In the final least-squares refinement, all non-hydrogen atoms except the carbon atoms comprising the two phenyl rings were refined anisotropically using the conventional 6-parameter thermal ellipsoid model. The phenyl carbon atoms were assigned single isotropic thermal parameters. Most of the hydrogen atoms were clearly revealed in difference electron density maps. All phenyl hydrogens were included in structure factor calculations in idealised positions assuming C-H 1.08 $\mathring{A}$. In each methyl group one hydrogen position was well defined and the remainder were included in idealised positions assuming C-H 1.10 $\mathring{A}$ and tetrahedral H-C-H angles. Refinement converged with $R_1 = 0.044$ and $R_2 = 0.043$. Analysis of F_o and F_c statistics indicated that for the most intense reflections, F_o values were systematically too low and that therefore secondary extinction was appreciable. This effect was corrected for, using the angularly dependent function derived by Zachariasen (1967) and incorporating it into the least-squares equations in the manner suggested by Larson (1970). In the final difference map there were no peaks of height greater than 0.51 eA^{-3} or one sixth of the average height of carbon atom peaks in earlier difference syntheses.

The function minimized in the least-squares refinement showed no systematic dependence on F_o or $\sin\theta$, and a calculation of the structure factors for the weak reflections not included in the refinement revealed no anomalies. The final parameters for all

Table 10.3a

ATOMIC PARAMETERS FOR N-(2-HYDROXYPHENYL) SALICYLALDIMINE DIMETHYL TIN(IV)

Atom	x	y	z	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Sn	0.0554(1)	0.1587(1)	0.0503(1)	0.0021(1)	0.0080(1)	0.0061(1)	0.0004(1)	0.0002(1)	0.0008(1)
O(1)	-0.0465(3)	0.0900(6)	0.0334(5)	0.0025(2)	0.0101(7)	0.0084(5)	0.0005(3)	0.0009(3)	0.0021(6)
O(2)	0.1370(3)	0.7837(7)	0.0928(6)	0.0022(7)	0.0089(8)	0.0148(3)	0.0004(4)	0.0001(3)	0.0043(7)
C(1)	0.0849(5)	0.040(1)	0.1686(8)	0.0033(3)	0.010(1)	0.0069(8)	0.0008(6)	0.0001(4)	0.0003(9)
C(2)	0.0791(5)	0.189(1)	-0.1076(8)	0.0029(4)	0.013(2)	0.0062(7)	0.0012(5)	0.0002(4)	0.0020(9)
N(1)	-0.0120(4)	0.3181(8)	0.0997(6)	0.0032(3)	0.009(1)	0.0051(6)	0.0007(5)	0.0004(3)	0.0009(7)
C(3)	0.0078(6)	0.430(1)	0.1214(8)	0.0040(4)	0.010(1)	0.0046(8)	0.0008(7)	0.0005(4)	0.0001(9)
C(11)	-0.0987(5)	0.184(1)	0.0667(6)	3.7(2)					
C(12)	-0.1658(5)	0.1186(9)	0.0644(7)	3.8(2)					
C(13)	-0.2196(6)	0.199(1)	0.0974(8)	5.0(2)					
C(14)	-0.2052(5)	0.317(1)	0.1328(8)	4.9(2)					
C(15)	-0.1381(5)	0.362(1)	0.1355(7)	4.4(2)					
C(16)	-0.0847(5)	0.284(1)	0.1018(7)	3.5(2)					
C(21)	0.1385(5)	0.404(1)	0.113(8)	4.4(2)					
C(22)	0.0776(4)	0.480(1)	0.1256(7)	3.9(2)					
C(23)	0.0834(5)	0.608(1)	0.1514(8)	5.0(2)					
C(24)	0.1473(5)	0.665(1)	0.1599(8)	5.4(3)					

Thermal parameters are in the form of $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})]$

Table 10.3b

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

Sn	0.187(1)	0.214(1)	0.242(1)
O(1)	0.19(1)	0.240(9)	0.29(1)
O(2)	0.19(1)	0.21(1)	0.38(1)
C(1)	0.22(2)	0.25(2)	0.26(1)
C(2)	0.21(2)	0.23(1)	0.29(2)
C(3)	0.20(1)	0.21(1)	0.26(1)
N	0.20(2)	0.24(2)	0.28(2)

atoms are given in Table 10.3a while the root-mean-square amplitudes of vibration of those atoms refined anisotropically are given in Table 10.3b. Structure factors are given in Appendix A5. Anomalous dispersion corrections from Cromer (1965) were applied to the scattering factors for tin only.

10.4 RESULTS AND DISCUSSION

The crystal structure consists of monomeric units of N-(2-hydroxyphenyl)-salicylaldimine dimethyl tin(IV) packed 8 per unit cell. Figure 10.4 shows the overall molecular geometry and indicates that the Schiff base is indeed functioning as a tridentate ligand. Principal intramolecular distances and angles and their standard deviations are given in Table 10.4. The tridentate ligand is approximately planar but there are individual atom deviations of up to 0.2 Å from the mean plane through the ligand and the tin atom. The departure from exact planarity can be described in terms of the orientations of the phenyl rings whose planes are inclined at 10° to each other. They are twisted so that C(14) and C(15) of the first ring are inclined towards C(2), and C(23) and C(24) of the second ring are inclined towards C(1).

As has been generally observed in pentacoordinate tin complexes (Ho & Zuckerman, 1973), the geometry around the tin atom in $C_{15}H_{15}NO_2Sn$ is best described as distorted trigonal bipyramidal. The oxygen atoms are at the apices and the methyl carbon atoms and the nitrogen atom form the equatorial plane from which the tin atom is displaced by 0.08 Å. The geometry of the Schiff base ligand does however lead to a considerable departure from the ideal trigonal bipyramidal environment. Thus the angle O(1)-Sn-O(2) is reduced from the ideal 180° to 158.5°, as a consequence of both oxygen atoms being bent towards the nitrogen atom of the complex ligand and away from the two methyl groups. Also, in the equatorial plane, the angle C(1)-Sn-C(2) has opened out to 140°. A similar effect has been observed in

Figure 10.4

GENERAL VIEW OF ONE MOLECULE OF THE COMPLEX ILLUSTRATING THE DISTORTED TRIGONAL BIPYRAMIDAL ENVIRONMENT OF THE TIN ATOM

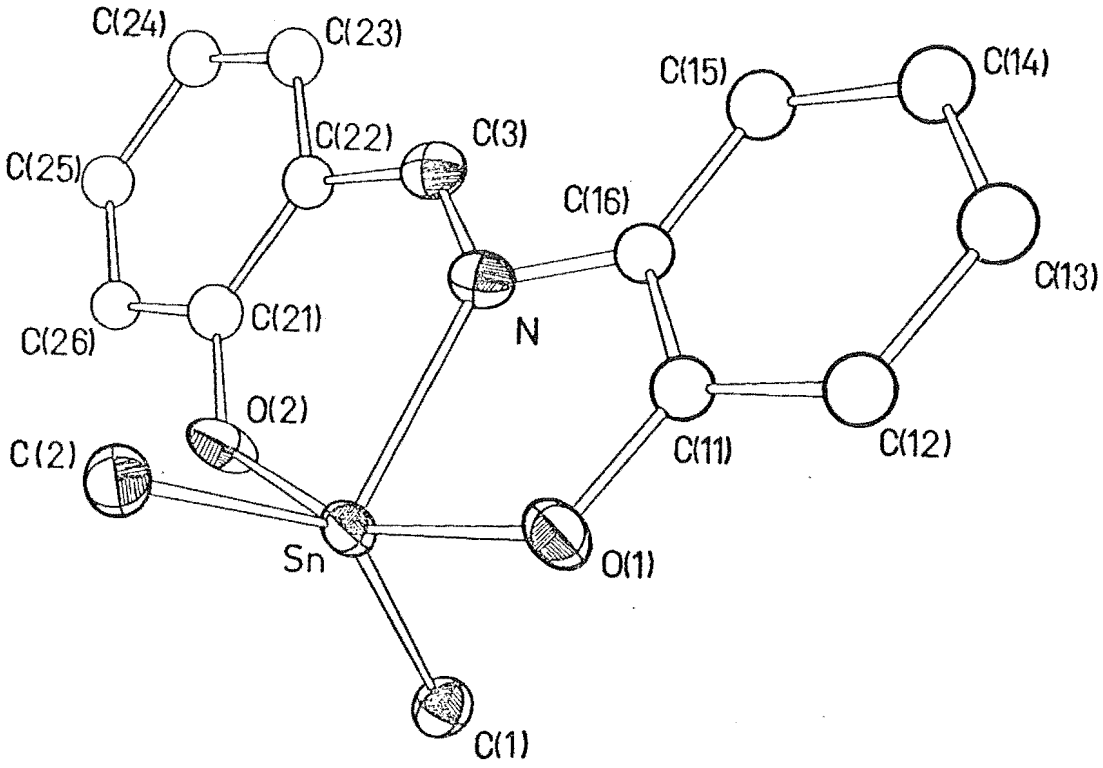


Table 10.4

BOND LENGTHS AND ANGLES

N-(2-HYDROXYPHENYL) SALICYLALDIMINE DIMETHYL TIN(IV)

Bond Length		Bond angle	
Sn-O(1)	2.108(6) Å	C(1)-Sn-C(2)	139.6(4)°
Sn-O(2)	2.130(7)	C(1)-Sn-N	112.5(3)
Sn-C(1)	2.10(1)	C(2)-Sn-N	107.3(4)
Sn-C(2)	2.12(1)	C(1)-Sn-O(2)	158.2(2)
Sn-N	2.225(8)	O(1)-Sn-C(1)	97.0(3)
O(1)-C(11)	1.35(1)	O(1)-Sn-C(2)	98.6(3)
O(2)-C(21)	1.30(1)	O(1)-Sn-N	75.3(3)
N-C(3)	1.27(1)	O(2)-Sn-C(1)	88.0(4)
N-C(16)	1.45(1)	O(2)-Sn-C(2)	90.2(3)
C(3)-C(22)	1.45(1)	O(2)-Sn-N	83.4(3)
C-C(phenyl)		Sn-O(1)-C(11)	117.6(6)
mean of 12 bonds	1.39(1)	Sn-O(2)-C(21)	132.5(6)
range	1.366 to 1.434	Sn-N-C(3)	126.2(8)
		Sn-N-C(16)	112.6(6)
		N-C(3)-C(22)	128.8(8)
		C(3)-N-C(16)	121.2(9)
		C-C-C(phenyl)	
		mean of 12 angles	120.0(9)
		range	117.3 to 121.2

the $[(CH_3)_2SnCl_3]^-$ anion (Einstein & Penfold, 1968) where, as in the present compound, there are only two methyl groups and one more highly electronegative ligand (a chlorine atom) in the equatorial positions.

Hitherto, nitrogen coordinated to tin in bipyramidal pentacoordinate compounds, has invariably occupied axial positions. It is now well established that, for a given type of bond in this type of coordination, axial bonds tend to be longer than equatorial bonds (e.g. Ho & Zuckerman, 1973). The Sn-N axial bonds listed by Chow (1971) are within the range 2.34-2.49 Å with the exception of the bond in $(CH_3)_3SnNCS$ (Forder & Sheldrick, 1970) which is 2.15(6) Å. While the large error in this measurement makes any conclusion suspect it should also be noted that the second axial bond in the compound, Sn-S is very long (3.13 Å) and must be very weak indeed. The equatorial Sn-N length of 2.225(8) Å observed in the present compound may therefore be said to conform to the general pattern in being significantly shorter than those axial Sn-N bonds with which direct comparison is possible.

CHAPTER 11

THE ISOMERIC CONFORMATIONS OF THE HEXA-μ-DITHIOCACODYLATO TETRAZINCSULPHIDE MOLECULES

11.1 INTRODUCTION

The hexa-μ-dithiocacodylato tetrazincsulphide molecules are a group of conformational isomers. The zinc atoms are tetrahedrally arranged about a central sulphur atom. The central sulphur atom, taken in turn with each of the six possible pairs of zinc atoms, is at the centre of six fused cyclohexane type rings. If these have conventional boat and chair conformations the conceivable distributions range from six chairs or boats to three of each. There are ten such possibilities detailed in Table 11.1b. Each zinc atom is shared between three rings and this association may prevent the occurrence of some of these possibilities.

The full symmetry of the tetrahedron imposes an overall regime of symmetry on the molecule. That is to say, any symmetry the molecule may possess must be a subset of that of the tetrahedron. The presence of a three-fold axis of symmetry would imply a six-boat, six-chair or three-boat,three-chair configuration. Mirror plane symmetry would require at least one one ring to be planar.

The four-fold inversion axis of symmetry of an exact tetrahedron could only be found in a four-chair, two-boat (or vice versa combination). Thus symmetry considerations help identify some possible conformational details in different isomers.

Furthermore the presence of symmetry is indicative of portions of a molecule making equal contributions to the potential energy of the whole molecule. Symmetrical molecules have a lower entropy than asymmetrical ones, so are less likely to occur. That they do occur, indicates that the minimisation of potential energy dominates the tendency to maximisation of entropy in such cases, and that the tendency to equipartition of potential energy is also important. In a system such as this, where six

bridging ligands, may individually, alternately, take on chair and boat configurations in the free state, a number of local potential energy minima, corresponding to different isomers, may exist. This is illustrated by the fact that different isomers have been crystallised for this complex. The probability that any particular isomer will form depends on the environment in which crystallisation takes place, and the number of ways of arranging ligands, in chair and boat forms, which result in each possible isomer. The second of these factors can be calculated in a strict combinatorial sense and values are given in Table 11.1a. Some of the possible arrangements may be impossible to obtain, with sensible chemical geometry and low potential energy.

Table 11.1a

CONFORMATIONS OF CHAIRS AND BOATS (c=chair, b=boat)

Configuration	3c 3b	4c 2b	2c 4b	5c 1b	1c 5b	6c	6b
Number of ways	20	15	15	6	6	1	1

The possible isomeric forms may be represented schematically. The six edges of a regular tetrahedron are related, in pairs, by its 3 S_4 symmetry axes. When such a pairing is carried out for bridging ligands then the structural possibilities including those discussed above may be represented as shown in Table 11.1b.

Table 11.1b

POSSIBLE CONFIGURATIONS IN A 2 RING TYPE CLASSIFICATION

Molecular Forms With Possible Point Symmetry					Asymmetric Molecular Forms				
bbb	ccc	ccc	cbc	bcb	cbc	ccc	bcc	cbb	bcc
bbb	ccc	bbb	cbc	bcb	bbc	cbb	bbb	bbb	ccc

11.2 EXPERIMENTAL SECTION

The crystals are long, thin, needle-like in appearance and transparent in colour and were grown by recrystallisation of the hexagonal crystals obtained when the compound $(CH_3)_2As(S)SAs(CH_3)_2$ (Bunsen, 1843; Cameron & Trotter 1964) is reacted with $Zn(ClO_4)_2.6H_2O$ in ethanol or acetone. (Johnstone, Fergusson & Robinson 1972). Preliminary precession photographs of these crystals exhibited monoclinic symmetry and the systematic absences h0l h+l odd, 0k0 k odd uniquely indicate that the space group is $P2_1/n$. The density of the crystal was measured by flotation, $D_m = 2.00g\ cm^{-3}$. Least-squares refinement of the cell constants as $\underline{a} = 32.508(12)$, $\underline{b} = 18.489(7)$, $\underline{c} = 30.589(12)$ Å, $\beta = 95.70(2)^o$ yields a calculated density of $1.90g\ cm^{-3}$ with four molecules in each asymmetric unit of the unit cell.

Zr filtered Mo radiation ($\lambda = .7107$ Å) was used. Data was collected from the positive k and l region of reciprocal space with $\theta < 15^o$ using an Hilger and Watts automatic diffractometer 48 step, single second, 0.01^o scan with 12 second background counts at each end of the scan. The intensities of 3 standard reflections were monitored every 100 reflections and the data scaled accordingly. Lorentz and polarisation corrections were applied. Of the 5176 reflections measured 735 had intensities $>3\sigma$, 1355 $> 2\sigma$ and 2742 $> \sigma$.

11.3 STRUCTURE DETERMINATION AND REFINEMENT

A structure containing forty arsenic and zinc atoms, fifty-two sulphur atoms and forty-eight carbon atoms, that is, a total of one hundred and forty non-hydrogen atoms having 560 variable parameters is reasonably large. Furthermore, the quantity of high quality data was not proportionately large. A variety of techniques were applied in the solution of this structure. Patterson and direct methods were applied in obtaining phases giving acceptable structural parameters. The principal problem arising was that of imperfect phasing giving rise to spurious peaks yielding apparently polymeric structures. The computer

program PATINV (described in Chapter 12) was developed to help search for the best solution strategy. Its first function was to test the model for consistency with the Patterson Map, with which it agreed very well. The vectors between spurious 'atoms', and between them and the molecules, were the same as those obtaining within the molecules, so this test did not provide the desired discrimination. Using the atomic superposition option a model identical to some of those already obtained by direct methods resulted.

The structure was eventually elucidated using the 1974 edition of MULTAN (Main, Woolfson & Germain). 58 atoms were located based on the phasing of the 500 reflections having highest E values. Apart from carbon and hydrogen atoms the positions of all but 4 of the remaining sulphur atoms were obtained by difference Fourier calculations following least-squares refinements of the model the positions of the remaining atoms were calculated. The refinements had to be done in blocks. Between cycles the variance of the bond lengths of the bond types present were calculated using the program BONDSTAT (see section 12.4). The strategy used, particularly in the late and expensive refinements, was to vary those blocks where the variance was greatest. The blocks of parameters varied were those pertaining to individual molecules. When temperature factors as well as positional parameters were refined some of the temperature factors became negative, and the lowest value of R_1 obtained was 0.20. On the other hand, when temperature factors were held at the constant values indicated in Tables 11.3a,b,c and d the lowest value of R_1 obtained was 0.24. Structure factors for this latter case are given in Appendix A6. The quality of the data did not merit further expenditure.

11.4 DESCRIPTION AND DISCUSSION OF THE STRUCTURE

In 1972 Johnstone, Fergusson and Robinson reported the formation of a three chair, three boat hexa-μ-dithiocacodylato tetrazincsulphide complex and the preparation by recrystallisation

Table 11.3a

ATOMIC PARAMETERS FOR $[SZn_4\{AsS_2(CH_3)_2\}_6]$ (1)

Atom	x	y	z	B
S(1)	0.265(3)	0.226(6)	0.677(4)	3.50
Zn(11)	0.289(1)	0.339(2)	0.643(2)	2.00
Zn(21)	0.306(1)	0.139(2)	0.654(2)	2.00
Zn(31)	0.207(1)	0.215(2)	0.652(1)	2.00
Zn(41)	0.276(2)	0.241(2)	0.758(2)	2.00
As(11)	0.332(1)	0.409(2)	0.747(1)	2.00
As(21)	0.321(1)	0.073(2)	0.766(1)	2.00
As(31)	0.161(1)	0.261(2)	0.757(1)	2.00
As(41)	0.360(1)	0.251(2)	0.587(1)	2.00
As(51)	0.216(1)	0.046(2)	0.604(1)	2.00
As(61)	0.205(1)	0.374(2)	0.582(1)	2.00
S(111)	0.359(3)	0.384(6)	0.682(3)	3.50
S(141)	0.346(3)	0.318(6)	0.793(3)	3.50
S(221)	0.313(3)	0.032(6)	0.694(3)	3.50
S(241)	0.289(3)	0.131(6)	0.786(4)	3.50
S(331)	0.139(3)	0.281(6)	0.690(3)	3.50
S(341)	0.207(3)	0.319(6)	0.776(3)	3.50
S(521)	0.272(3)	0.099(6)	0.590(4)	3.50
S(531)	0.180(4)	0.105(6)	0.651(4)	3.50
S(611)	0.238(4)	0.410(6)	0.638(4)	3.50
S(631)	0.195(3)	0.260(6)	0.579(3)	3.50
C(111)	0.272	0.418	0.735	4.00
C(112)	0.355	0.502	0.768	4.00
C(211)	0.376	0.119	0.773	4.00
C(212)	0.322	-0.011	0.806	4.00
C(311)	0.117	0.276	0.795	4.00
C(312)	0.178	0.158	0.760	4.00
C(411)	0.412	0.307	0.591	4.00
C(412)	0.360	0.188	0.535	4.00
C(511)	0.234	-0.046	0.631	4.00
C(512)	0.180	0.026	0.550	4.00
C(611)	0.236	0.399	0.534	4.00
C(612)	0.152	0.422	0.576	4.00

Table 11.3b

ATOMIC PARAMETERS FOR $[SZn_4\{AsS_2(CH_3)_2\}_6]$ (2)

Atom	x	y	z	B
S(2)	0.418(4)	0.229(6)	0.001(4)	3.50
Zn(12)	0.422(1)	0.230(2)	0.077(1)	2.00
Zn(22)	0.482(2)	0.241(2)	-0.028(2)	2.00
Zn(32)	0.375(1)	0.342(2)	-0.018(1)	2.00
Zn(42)	0.383(1)	0.121(3)	-0.028(1)	2.00
As(12)	0.390(1)	0.051(2)	0.082(1)	2.00
As(22)	0.470(1)	0.095(2)	-0.095(1)	2.00
As(32)	0.293(1)	0.229(2)	-0.054(1)	2.00
As(42)	0.548(1)	0.234(2)	0.086(1)	2.00
As(52)	0.455(1)	0.412(2)	-0.077(1)	2.00
As(62)	0.372(1)	0.394(2)	0.089(1)	2.00
S(112)	0.436(3)	0.113(6)	0.118(3)	3.50
S(142)	0.406(4)	0.028(6)	0.028(4)	3.50
S(222)	0.508(3)	0.202(6)	-0.105(3)	3.50
S(242)	0.402(4)	0.119(6)	-0.095(4)	3.50
S(332)	0.301(3)	0.330(6)	-0.020(4)	3.50
S(342)	0.315(3)	0.129(6)	-0.031(3)	3.50
S(412)	0.488(4)	0.303(6)	0.101(4)	3.50
S(422)	0.533(3)	0.168(6)	0.035(3)	3.50
S(522)	0.509(3)	0.360(6)	-0.025(3)	3.50
S(532)	0.391(3)	0.387(6)	-0.086(3)	3.50
S(612)	0.373(3)	0.293(6)	0.109(3)	3.50
S(632)	0.406(3)	0.437(6)	0.035(4)	3.50
C(121)	0.379	-0.037	0.113	4.00
C(122)	0.340	0.109	0.073	4.00
C(221)	0.492	0.049	-0.039	4.00
C(222)	0.476	0.027	-0.143	4.00
C(321)	0.233	0.211	-0.064	4.00
C(322)	0.315	0.237	-0.111	4.00
C(421)	0.567	0.178	0.139	4.00
C(422)	0.592	0.299	0.072	4.00
C(521)	0.472	0.397	-0.135	4.00
C(522)	0.455	0.524	-0.062	4.00
C(621)	0.393	0.450	0.143	4.00
C(622)	0.313	0.419	0.076	4.00

Table 11.3c

ATOMIC PARAMETERS FOR $[SZn_4\{AsS_2(CH_3)_2\}_6]$ (3)

Atom	x	y	z	B
S(3)	0.725(3)	0.272(6)	0.816(4)	3.50
Zn(13)	0.689(1)	0.169(2)	0.844(1)	2.00
Zn(23)	0.801(1)	0.253(2)	0.849(1)	2.00
Zn(33)	0.708(1)	0.363(2)	0.857(2)	2.00
Zn(43)	0.726(2)	0.278(2)	0.742(2)	2.00
As(13)	0.661(1)	0.111(2)	0.732(1)	2.00
As(23)	0.833(1)	0.293(2)	0.741(1)	2.00
As(33)	0.667(1)	0.438(2)	0.753(1)	2.00
As(43)	0.778(1)	0.073(2)	0.899(1)	2.00
As(53)	0.810(1)	0.397(2)	0.917(1)	2.00
As(63)	0.628(1)	0.277(2)	0.909(1)	2.00
S(113)	0.672(3)	0.071(6)	0.796(3)	3.50
S(143)	0.724(3)	0.160(6)	0.702(4)	3.50
S(223)	0.842(3)	0.311(6)	0.820(4)	3.50
S(243)	0.774(3)	0.330(6)	0.709(3)	3.50
S(333)	0.654(3)	0.414(6)	0.821(3)	3.50
S(343)	0.675(3)	0.344(6)	0.717(4)	3.50
S(413)	0.721(3)	0.120(6)	0.916(4)	3.50
S(423)	0.816(4)	0.117(6)	0.850(4)	3.50
S(523)	0.819(3)	0.296(6)	0.920(4)	3.50
S(533)	0.760(4)	0.442(6)	0.868(4)	3.50
S(613)	0.616(3)	0.208(6)	0.854(3)	3.50
S(633)	0.690(4)	0.328(6)	0.928(4)	3.50
C(131)	0.619	0.187	0.729	4.00
C(132)	0.641	0.030	0.695	4.00
C(231)	0.835	0.188	0.732	4.00
C(232)	0.878	0.339	0.715	4.00
C(331)	0.622	0.498	0.725	4.00
C(332)	0.719	0.492	0.752	4.00
C(431)	0.812	0.078	0.956	4.00
C(432)	0.769	-0.030	0.884	4.00
C(531)	0.863	0.439	0.903	4.00
C(532)	0.800	0.430	0.975	4.00
C(631)	0.618	0.224	0.960	4.00
C(632)	0.591	0.361	0.900	4.00

Table 11.3d

ATOMIC PARAMETERS FOR $[SZn_4\{AsS_2(CH_3)_2\}_6]$ (4)

Atom	x	y	z	B
S(4)	0.580(4)	0.261(6)	0.500(4)	3.50
Zn(14)	0.563(1)	0.268(2)	0.418(1)	2.00
Zn(24)	0.617(1)	0.367(3)	0.518(1)	2.00
Zn(34)	0.608(1)	0.158(2)	0.521(1)	2.00
Zn(44)	0.520(2)	0.266(2)	0.524(2)	2.00
As(14)	0.471(1)	0.292(2)	0.421(1)	2.00
As(24)	0.545(1)	0.417(2)	0.597(1)	2.00
As(34)	0.538(1)	0.092(2)	0.587(1)	2.00
As(44)	0.625(1)	0.428(2)	0.405(1)	2.00
As(54)	0.698(1)	0.257(2)	0.565(1)	2.00
As(64)	0.597(1)	0.079(2)	0.415(1)	2.00
S(114)	0.516(4)	0.332(6)	0.395(4)	3.50
S(144)	0.465(3)	0.322(6)	0.496(3)	3.50
S(224)	0.610(3)	0.424(6)	0.589(4)	3.50
S(244)	0.514(3)	0.322(6)	0.600(3)	3.50
S(334)	0.589(4)	0.125(6)	0.594(4)	3.50
S(344)	0.485(3)	0.148(6)	0.546(3)	3.50
S(414)	0.635(3)	0.348(6)	0.389(4)	3.50
S(424)	0.607(3)	0.464(6)	0.463(4)	3.50
S(524)	0.684(3)	0.354(6)	0.519(4)	3.50
S(534)	0.663(3)	0.188(6)	0.508(3)	3.50
S(614)	0.556(3)	0.164(6)	0.390(3)	3.50
S(634)	0.605(3)	0.044(6)	0.491(4)	3.50
C(141)	0.420	0.327	0.386	4.00
C(142)	0.474	0.188	0.417	4.00
C(241)	0.535	0.466	0.652	4.00
C(242)	0.516	0.471	0.548	4.00
C(341)	0.545	-0.002	0.559	4.00
C(342)	0.519	0.078	0.645	4.00
C(441)	0.582	0.464	0.363	4.00
C(442)	0.676	0.478	0.400	4.00
C(541)	0.756	0.232	0.573	4.00
C(542)	0.673	0.259	0.619	4.00
C(641)	0.586	-0.009	0.380	4.00
C(642)	0.653	0.114	0.407	4.00

Figure 11.4a

STRUCTURE OF $[SZn_4\{AsS_2(CH_3)_2\}_6]$ JOHNSTONE ET AL.

(Three top rings are chairs, three bottom rings boats)

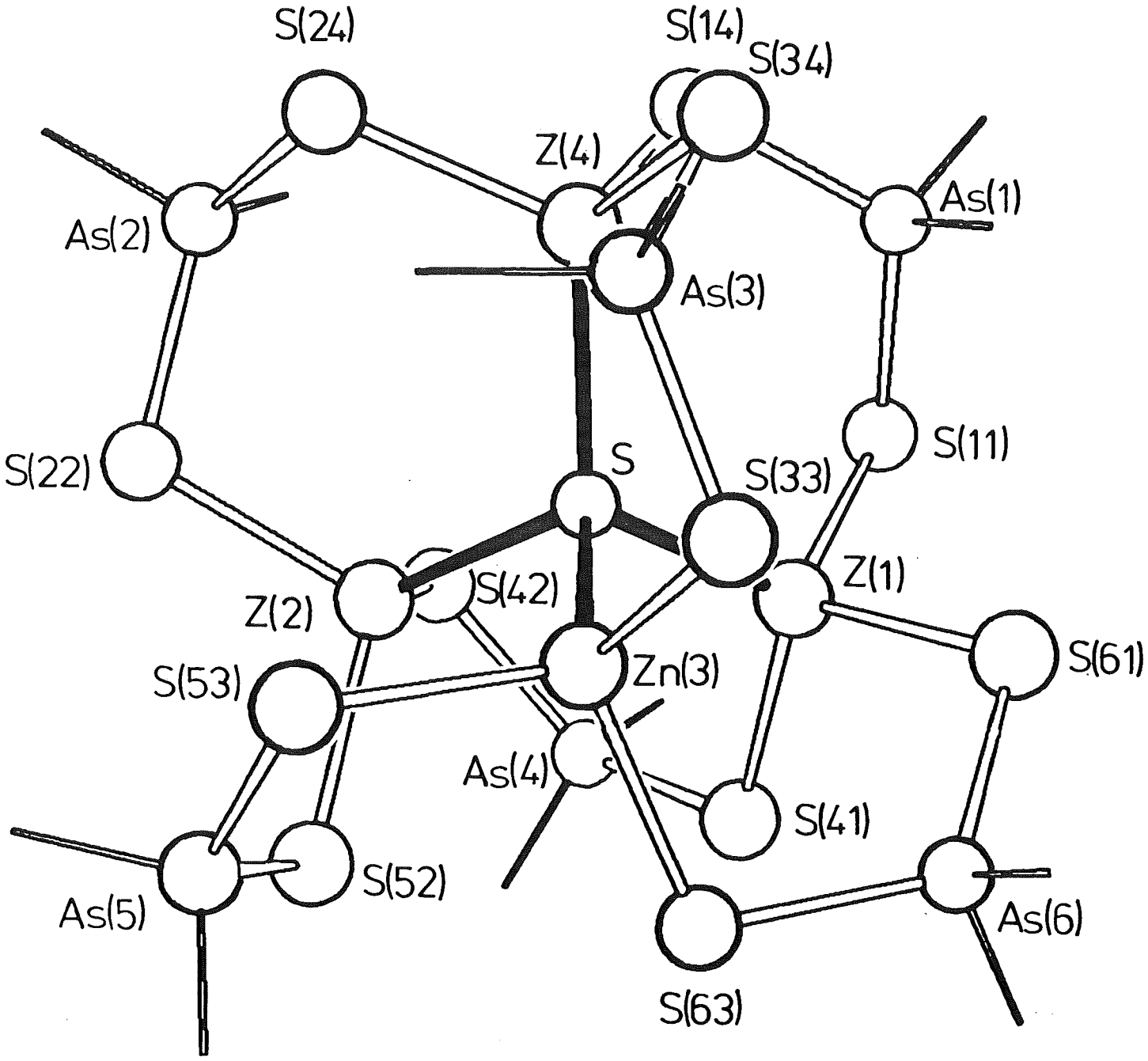
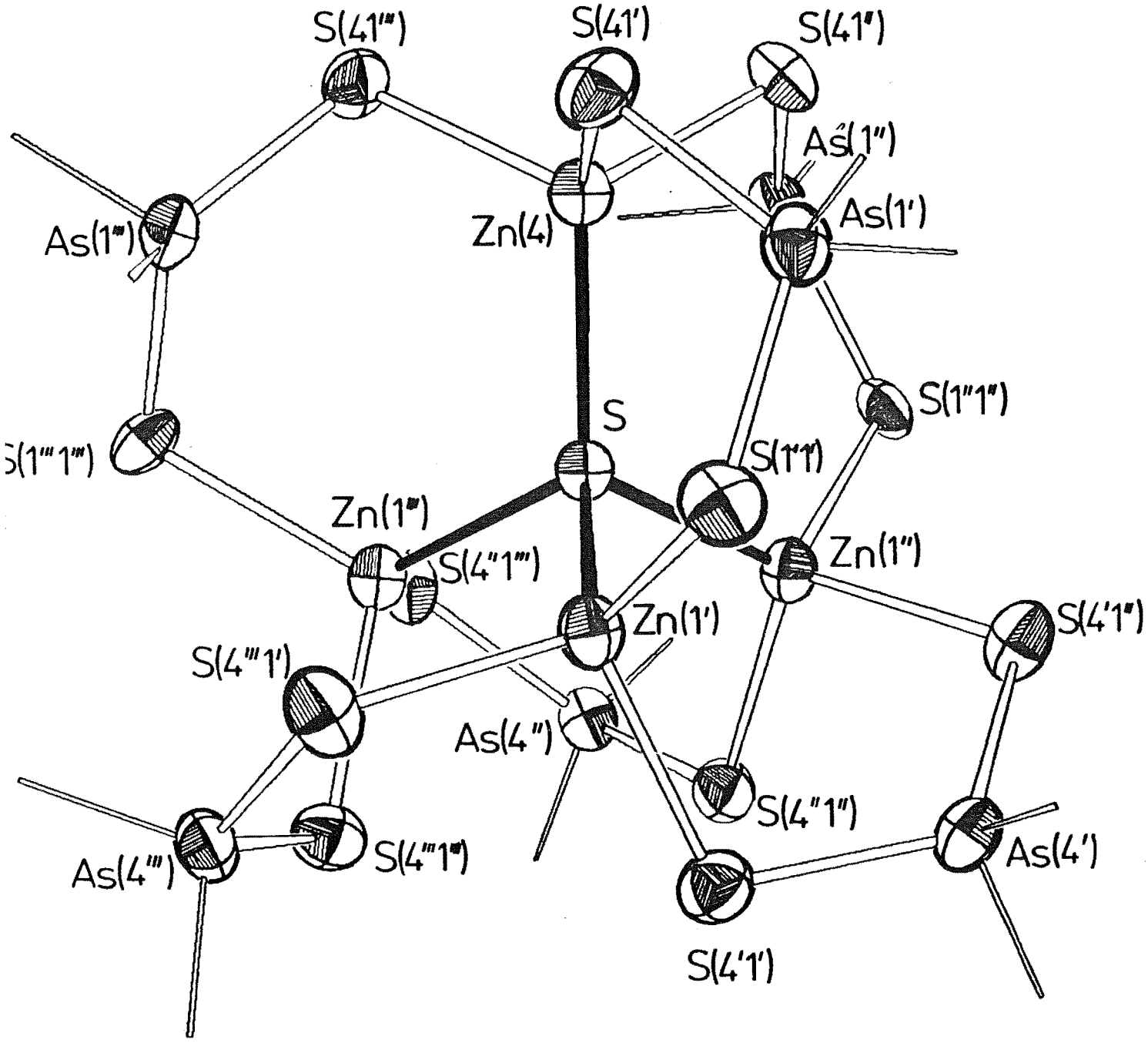


Figure 11.4b

STRUCTURE OF $[SZn_4\{AsS_2(CH_3)_2\}_6]$ BATES

(All rings are boats)



using other solvents, of three other crystalline forms. The molecule, shown in Figure 11.4a had approximately C_3 point group symmetry. The structure, shown in Figure 11.4b, of a second isomer consisting of six boats, has since been determined by Bates (1978) and also has C_3 (crystallographic) symmetry. If the sulphur atoms are designated either central or ring then the 'bow-stern' interatomic vectors of the boats are central sulphur-arsenic in three cases and ring sulphur-zinc in the three other cases. Boats and chairs have been distinguished by mean-plane calculations. The 1972 structure has twist-chairs in place of the central sulphur-arsenic boats, with 'head-toe' interatomic vectors in the same sense. The structure with space group $P2_1/n$ and Z = 16 discussed by Johnstone, Fergusson and Robinson is the subject of study here. In each asymmetric unit it has three molecules, shown in Figures 11.4c,d,e, with the three chair, three boat C_3 conformation and a fourth molecule, (see Figures 11.4f,f') itself the third conformational isomer discovered, with S_4 symmetry. That is, this fourth molecule is the fourth type indicated in Table 11.1b. Models can be made of the three isomers whose structures have been determined as well as the first of the asymmetric molecular forms in Table 11.1b. None of these show undue mechanical strain, nor unacceptable contact distances between the methyl groups. Of the crystalline forms originally obtained by Johnstone et al. only the one with hexagonal space group $P6_3$ has not been the subject of succesful structure determination.

It may be further pointed out that as the space group $P2_1/n$ has a centre of inversion, molecules in different asymmetric units must have enantiomorphic isomers in others, so there are twice as many isomers as may at first appear to be the case. That two different isomers should occur in the same asymmetric unit in the proportion 3:1 is extremely unusual. On the other hand, as has been discussed in 11.1, the compound is unusual in that it can potentially adopt a number of forms five of which are potentially

Figure 11.4c

STRUCTURE OF $[SZn_4\{AsS_2(CH_3)_2\}_6]$ MOLECULE (1)

(Three top rings are chairs, three bottom rings boats)

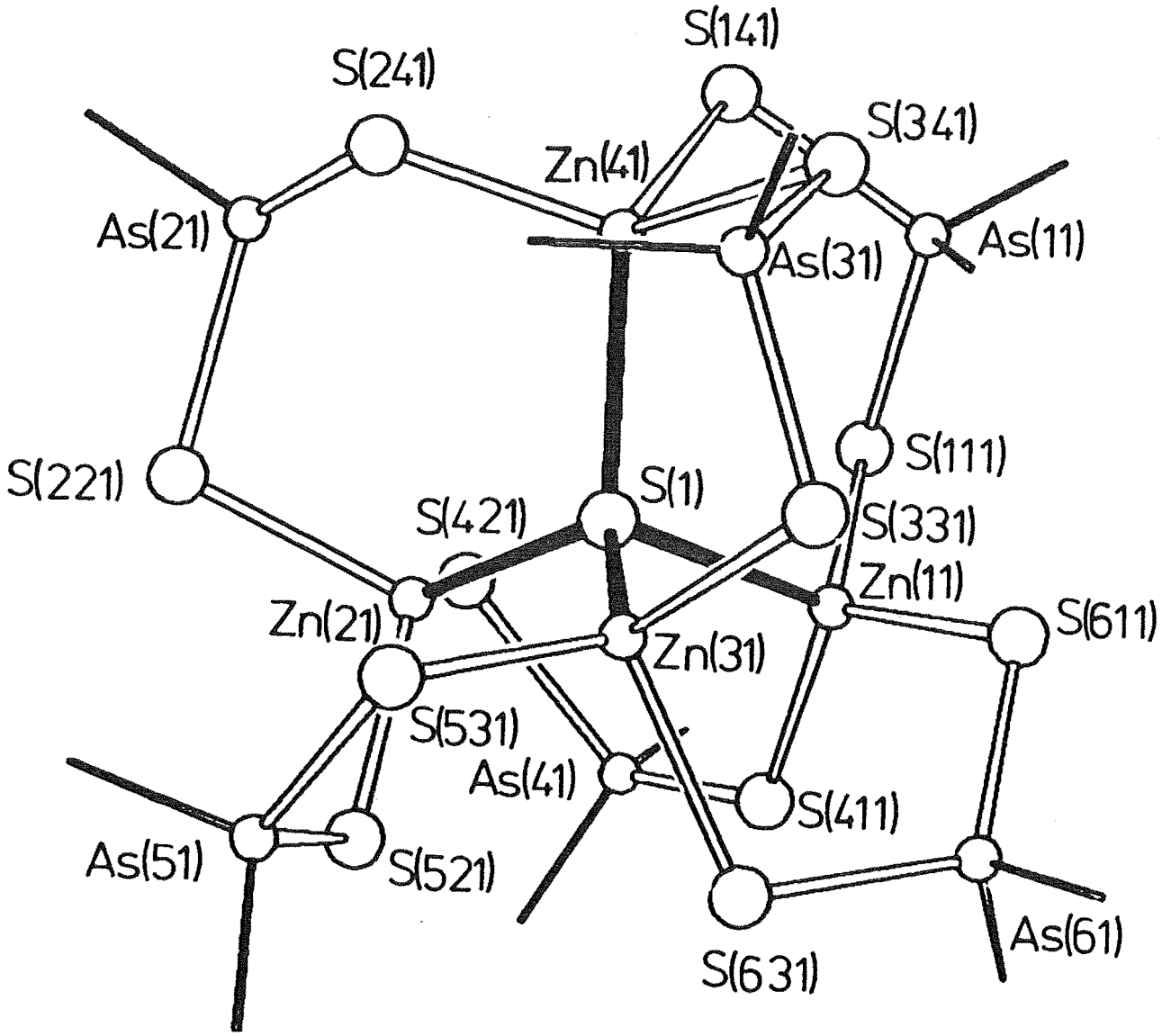


Figure 11.4d

STRUCTURE OF $[SZn_4\{AsS_2(CH_3)_2\}_6]$ MOLECULE (2)

(Three top rings are chairs, three bottom rings boats)

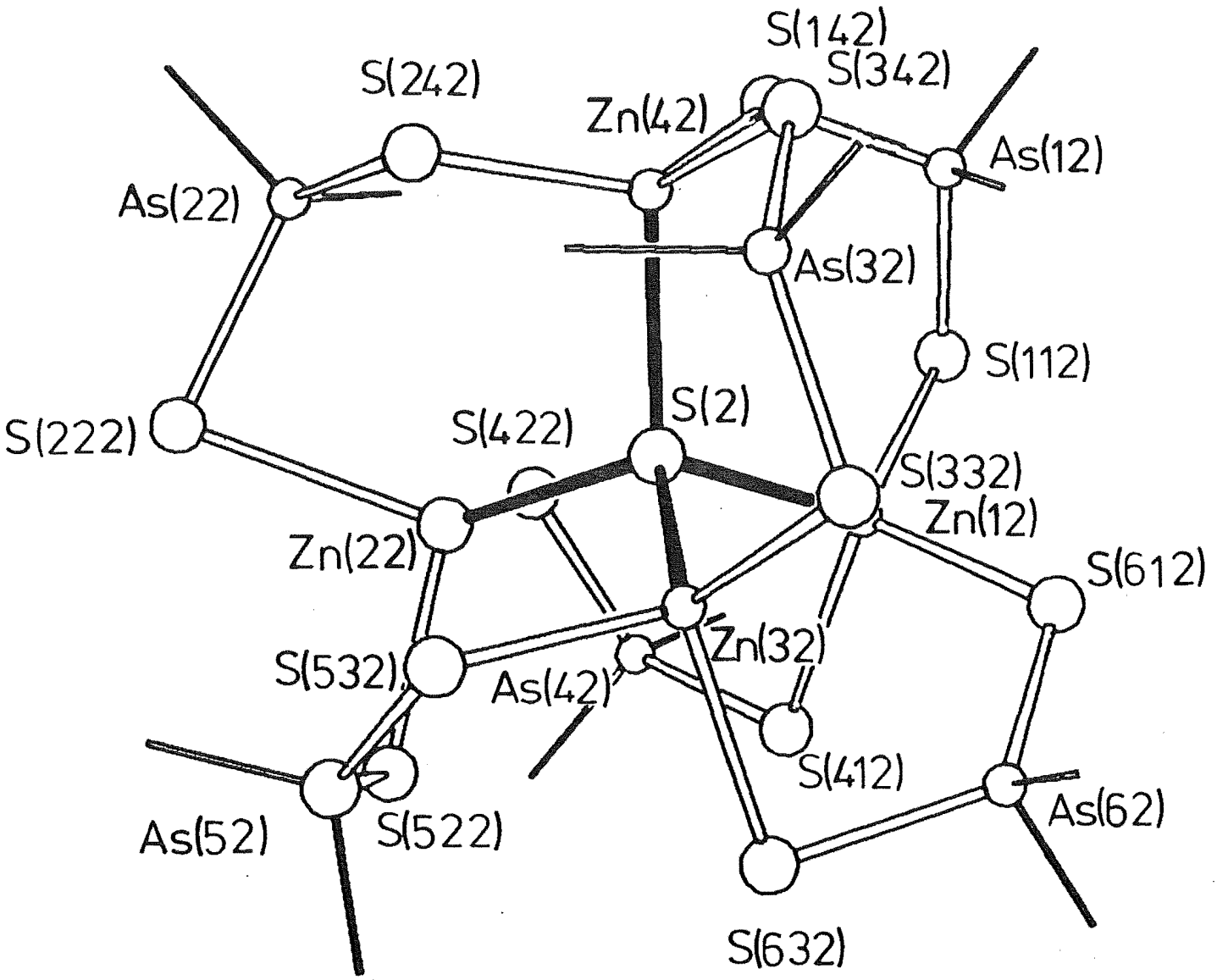


Figure 11.4e

STRUCTURE OF $[SZn_4\{AsS_2(CH_3)_2\}_6]$ MOLECULE (3)

(Three top rings are chairs, three bottom rings boats)

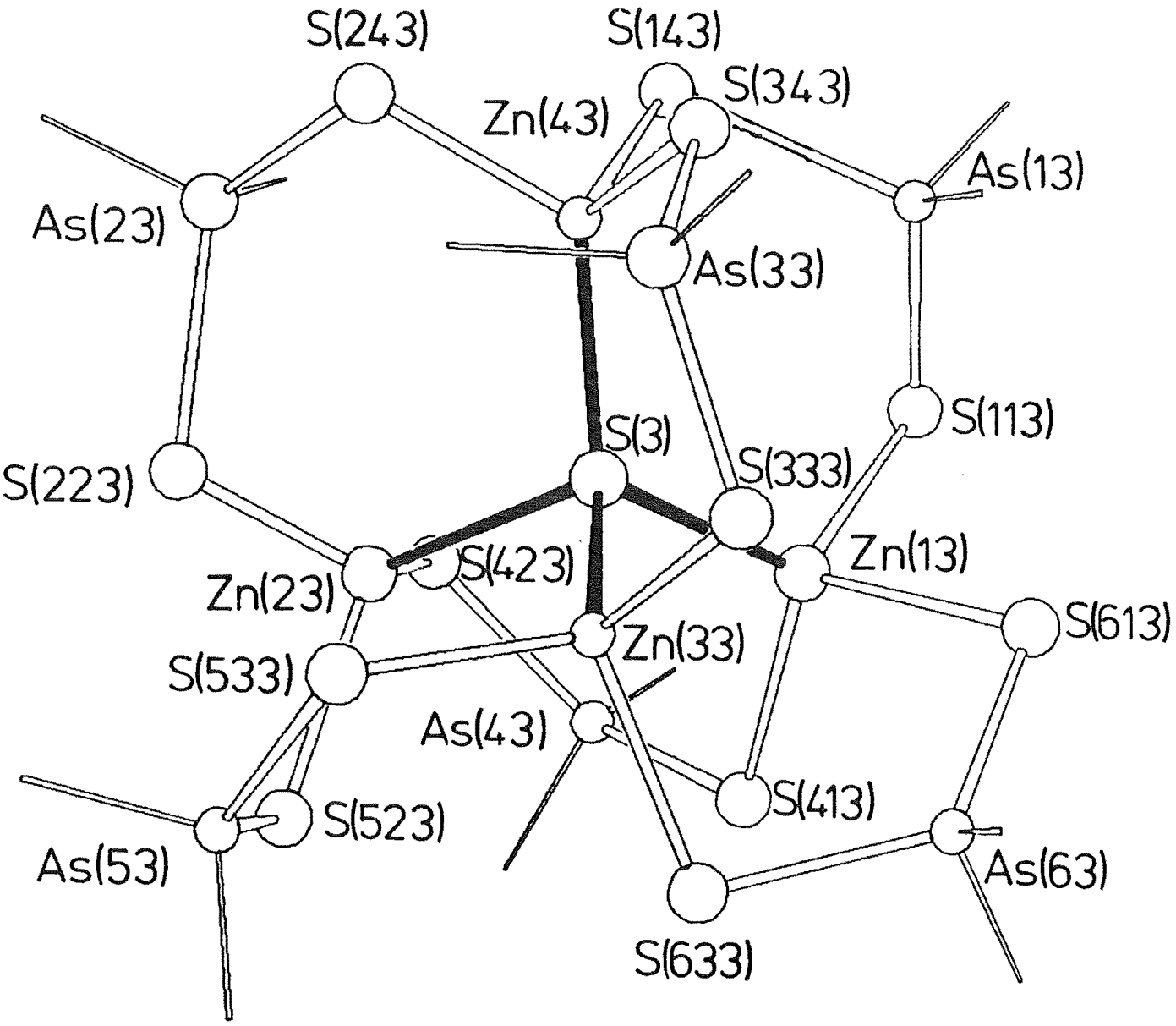


Figure 11.4f

STRUCTURE OF $[SZn_4\{AsS_2(CH_3)_2\}_6]$ MOLECULE (4)

(Four chairs and two boats)

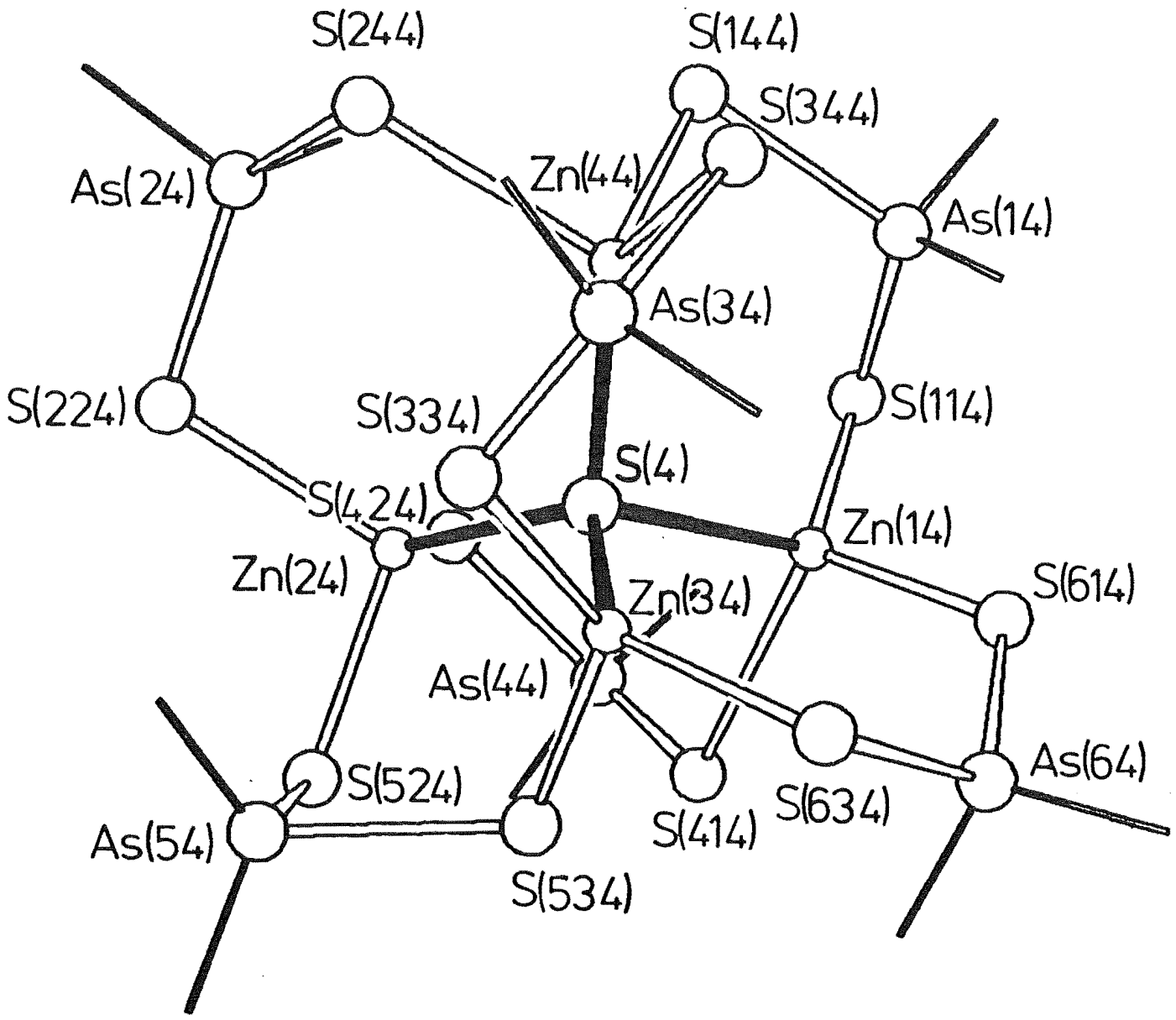
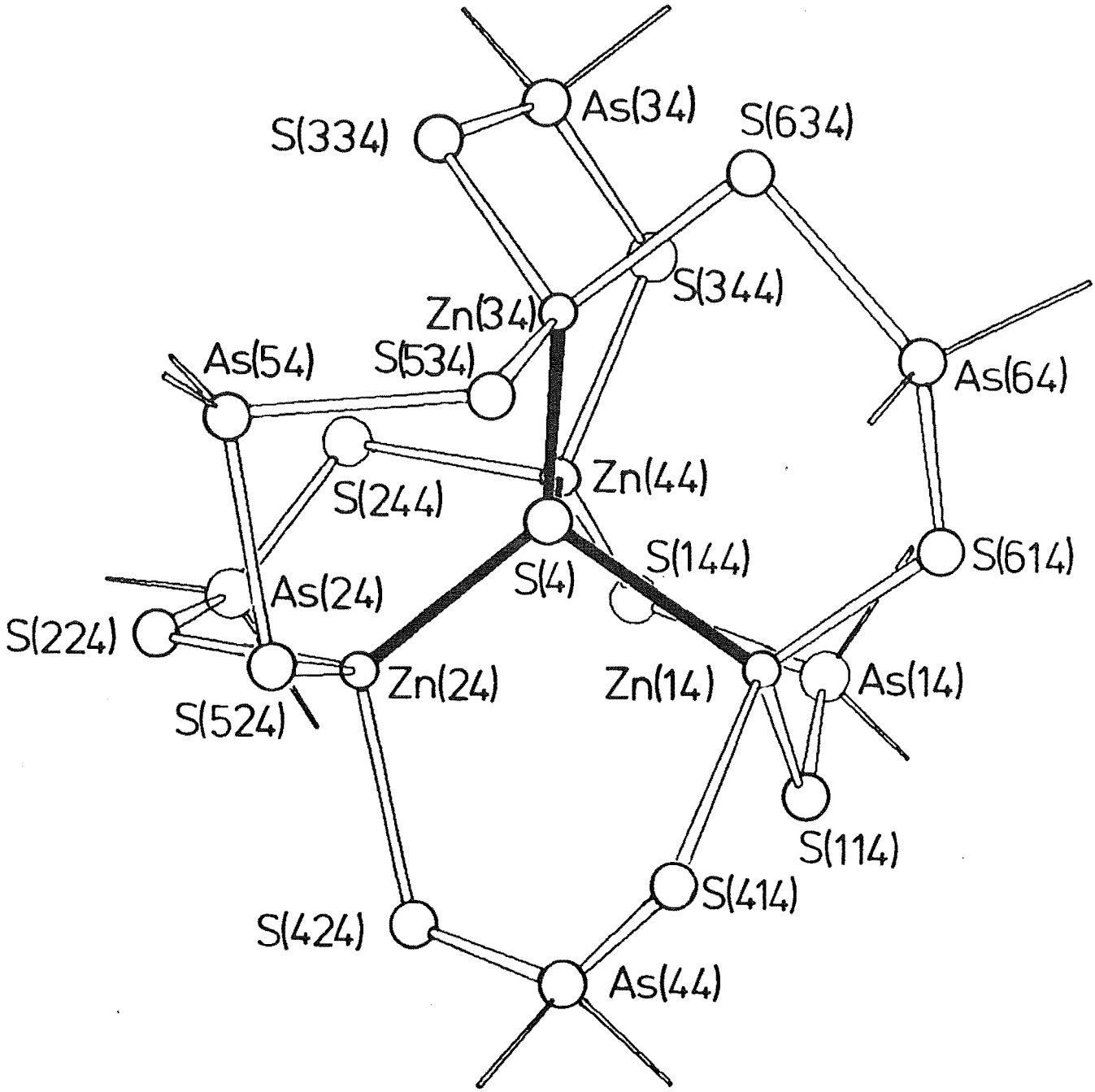


Figure 11.4f'

STRUCTURE OF $[SZn_4\{AsS_2(CH_3)_2\}_6]$ MOLECULE (4) ALT. VIEW

(Four chairs and two boats)



symmetric whilst others are definitely asymmetric. It is unlikely that the gradients of potential energy towards formation of the different isomeric forms will be of equal height or slope. If P_{ij} is defined as the probability of crystallisation of isomer i in solvent (environment) j. P_{ij} can then be represented as the product of two factors p_i and f_{ij} where p_i is the number of ways in which an isomer may form (as given in Table 11.1a) and f_{ij} is a formation factor for isomer i in environment j. In some environments it appears that for one particular value of i there is a value of P_{ij} close to 1.0, whilst in the case under study here there are two isomeric components. For this environment (recrystallisation of the hexagonal crystals from dichloromethane - di), j = di, for the three chair, three boat structure $P_{1di} = 20f_{1di}$, and for the four chair, two boat structure $P_{2di} = 15f_{2di}$. The observed ratio for P_{1di} : P_{2di} is 3:1 which taken with the above relationships implies that $f_{1di}/f_{2di} = 9/4$. This indicates that the paths taken by the molecules to potential energy minima on crystallisation as different isomers are unequal, and gives a guide to the effective overall differences.

Bond lengths and angles for the molecules are presented 'ring by ring' in Figures 11.4g,h,i and j. The range of values of bond lengths and angles reflects the poor quality of the data.

Figure 11.4g

DISTANCES AND ANGLES IN MOLECULE (1)

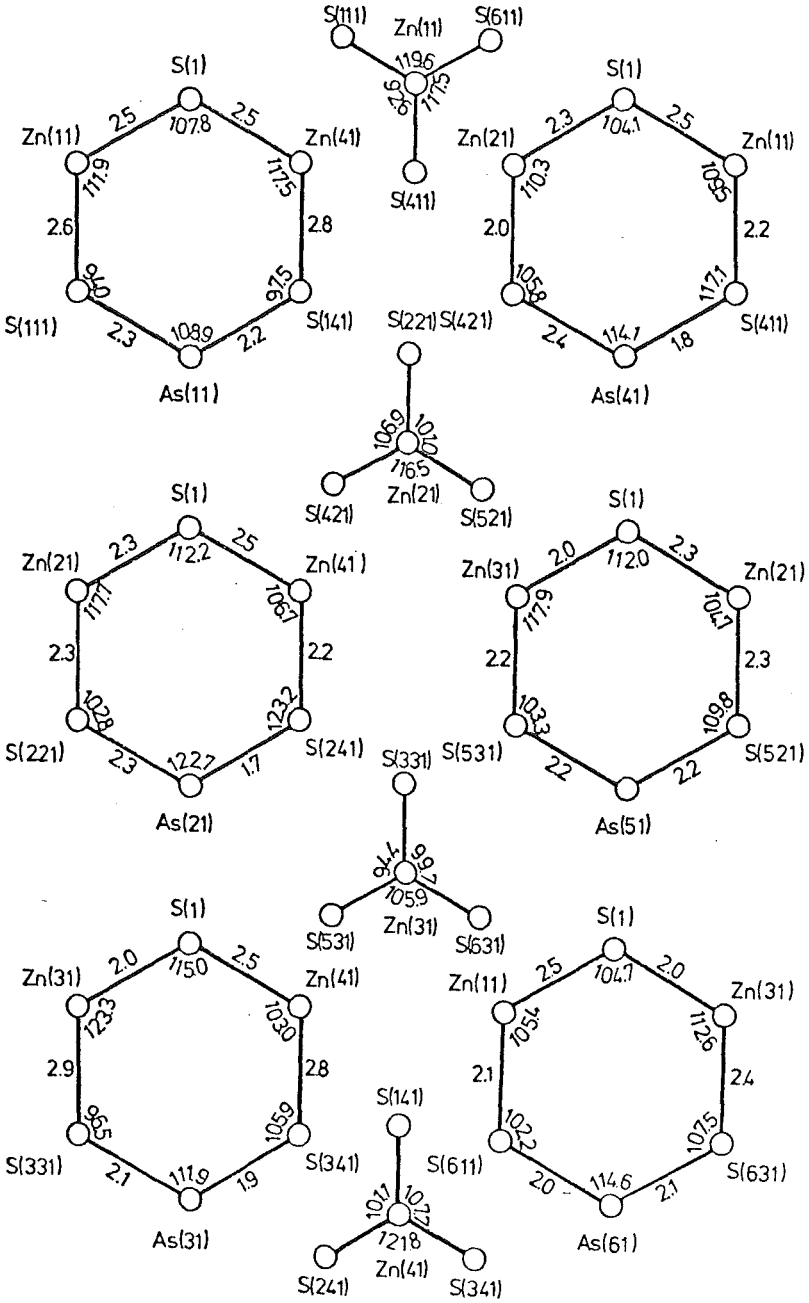


Figure 11.4h

DISTANCES AND ANGLES IN MOLECULE (2)

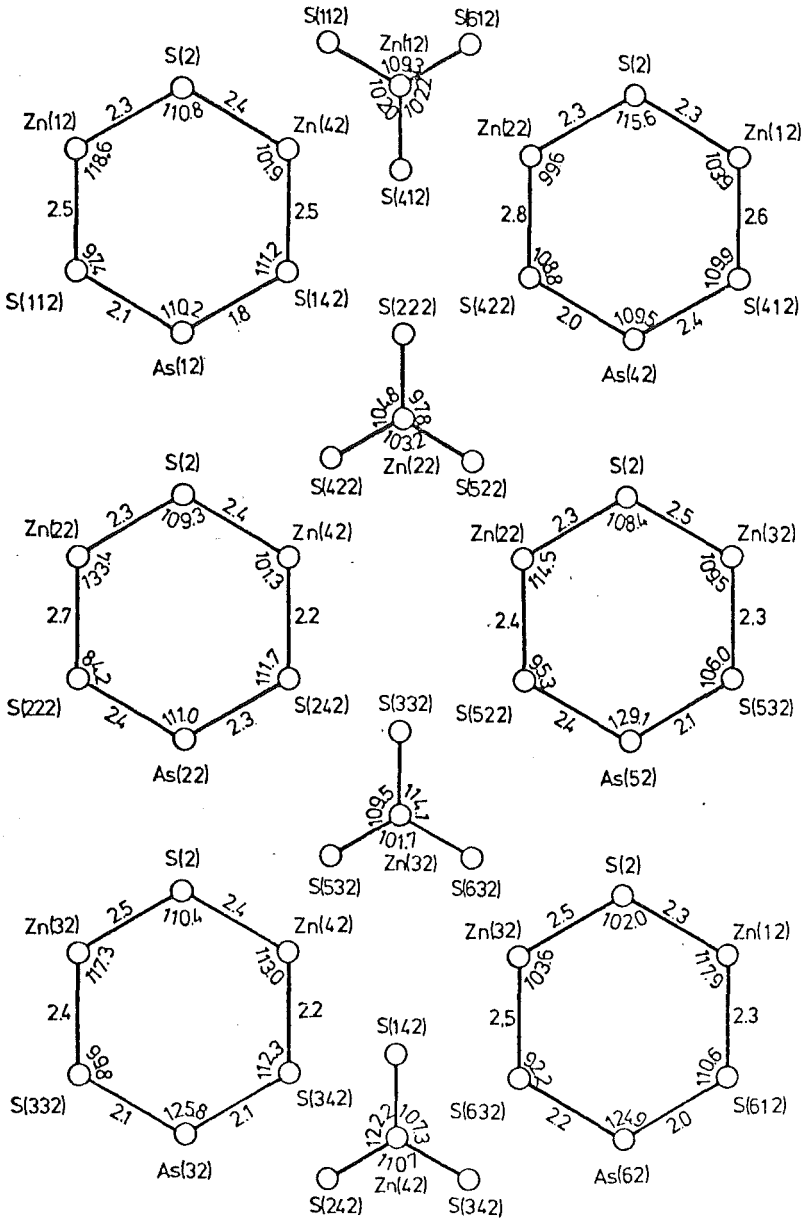


Figure 11.4i

DISTANCES AND ANGLES IN MOLECULE (3)

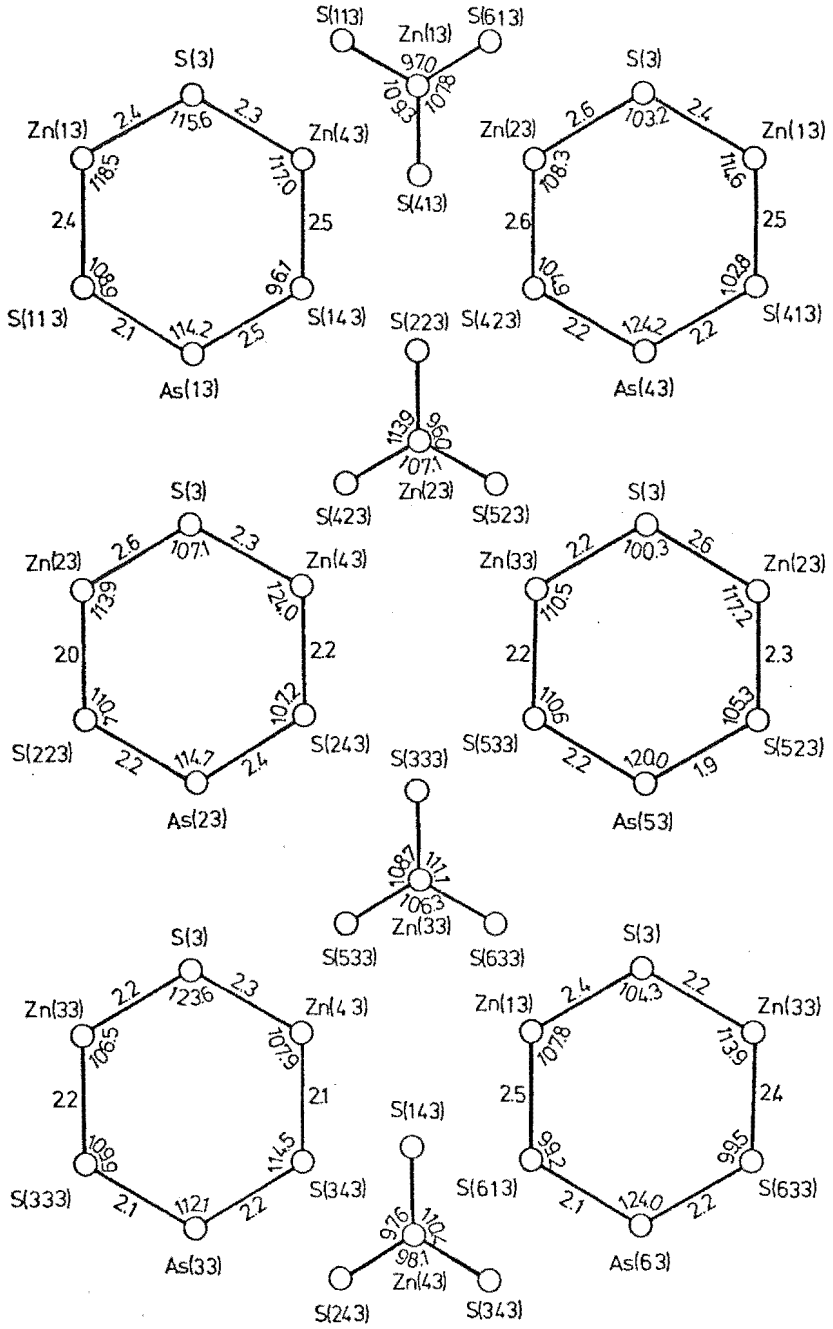
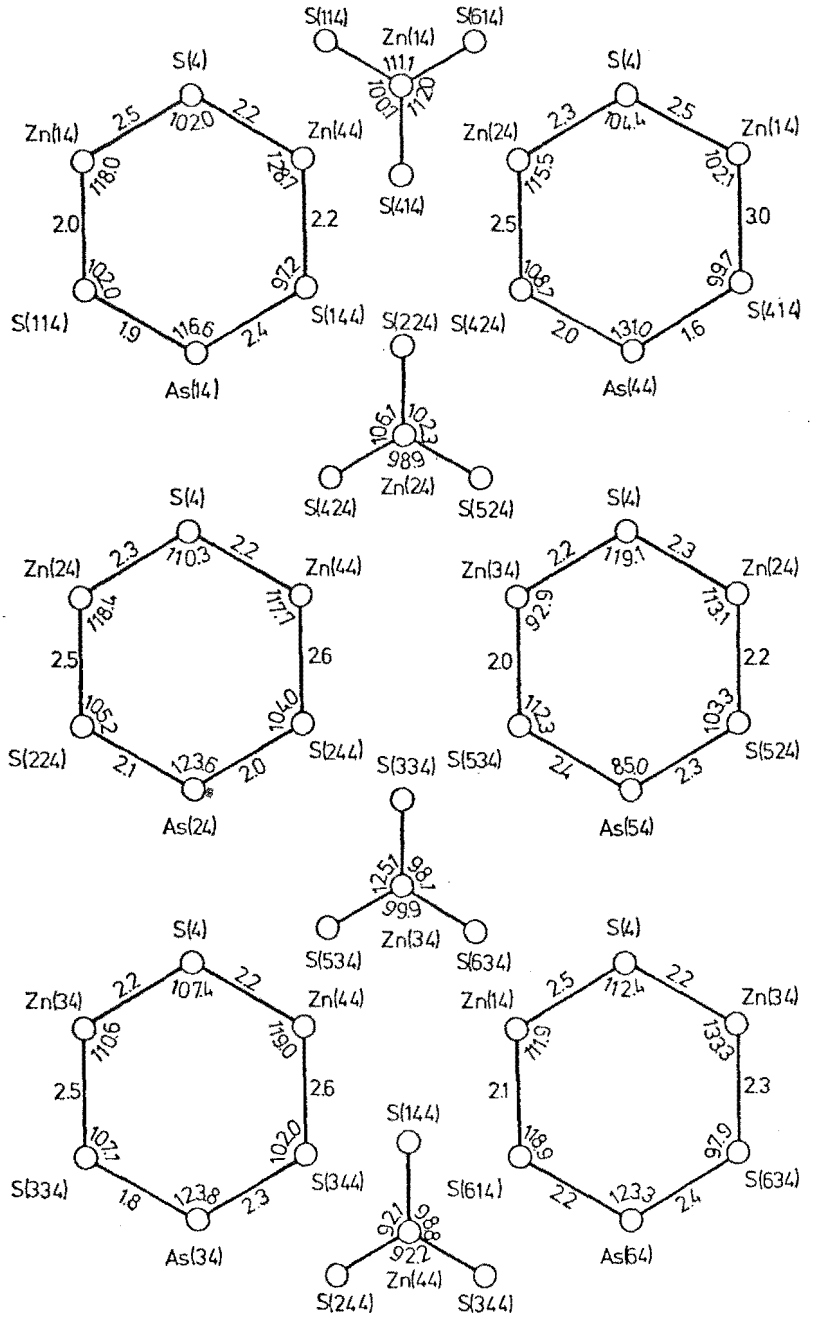


Figure 11.4j

DISTANCES AND ANGLES IN MOLECULE (4)



CHAPTER 12

COMPUTER PROGRAMS

12.1 INVESTIGATION OF PEAKS IN PATTERSON MAPS (PATINV)

12.1.1 INTRODUCTION

This program performs the following tasks:

(1) Obtains possible atomic positions using Harker planes and lines.

(2) Verifies the consistency of atomic positions of a proposed model with the Patterson peaks.

(3) Extends models by atomic superposition (using only peak positions).

12.1.2 INPUT

(1) Title

(2) Cell constants and control parameters.

(3) Patterson peak positions.

(4) Proposed atomic positions.

12.1.3 OBTAINING ATOMIC POSITIONS USING HARKER PLANES AND LINES

The N real space symmetry operations are used to obtain the M Patterson space symmetry operations by removing the translational components (and adding a centre of symmetry if necessary). The N space group symmetry operations are used to form the N(N-1)/2 possible differences between equivalent positions which may be on Harker lines or sections. This list is then reduced, to the unique set in which none are related by Patterson space group symmetry.

This set of Harker vectors is of the form $h_i = a_i + x_i$ $(i=1,3)$ and with each can be associated a vector $\underline{z}$ with components $z_i = \delta_{ij}$ $(i=1,3;\ j=1,3)$ where δ_{ij} is the Kronecker delta and $i = j$ iff $x_i = 0$. $(a_i = 0$ or $0.5)$

For any pair of vectors $\underline{z}_k$, $\underline{z}_m$ where $|\underline{z}_k + \underline{z}_m| > \sqrt{2}$ atomic

positions can be found provided that vectors of classes k and m exist in the Patterson map.

Consider the following Harker vector classes, and their associated z vectors

h_k = 1/2 + 2x, 1/2, 1/2 - 2z then $\underline{z}_k$ = (1,0,1)

and h_m = 0, 2y, 1/2 $\underline{z}_m$ = (0,1,0)

then $|\underline{z}_k + \underline{z}_m| = |(1,0,1) + (0,1,0)| = 3$, and so Harker vectors of these 2 types will be able to yield possible atomic coordinates.

For example, consider the two vectors in the Patterson map

$\underline{v}_k$ = 0.7 0.5 0.3

and $\underline{v}_m$ = 0.0 0.6 0.5

The solutions of

$$1/2 + 2x = 0.7$$
$$2y = 0.6$$
$$1/2 - 2z = 0.3$$

are calculated using modulo 1 arithmetic, as an ideal crystal structure is invariant with respect to unit cell translations. This leads to eight possible solutions each of which may be generated from the vector $\underline{p}$ = (0.1 0.3 0.1) by addition of 0.5 to any of the three coordinates.

The program lists the set of vectors $\underline{z}$ and the combinations of $\underline{z}_k$ and $\underline{z}_m$ found to be acceptable when all possible pairs of vectors in the map have been considered. Then the Patterson peak list is searched and the peaks classified according to their $\underline{z}$ character. The elements of classes of vectors taken two at a time are then combined to yield possible atomic positions p, only one of the eight possible positions being calculated at this point. If $|\underline{z}_l + \underline{z}_n| > \sqrt{2}$, as in the cases $\underline{z}'$ = (1,0,1) and $\underline{z}''$ = (0,1,1) then it is necessary that $p_3' = p_3''$.

A lot of the atomic positions 'found' will not be genuine, so the number is reduced by accepting only those identical positions, $\underline{p}$ and $\underline{p}'$, which arise from two distinct pairs of $\underline{z}$ classes. (Identity is established by equality of $2\underline{p}$ and $2\underline{p}'$, to overcome the ambiguity of 0.5 in each coordinate). Note that the

pair $\underline{z}$, $\underline{0}$ is acceptable provided as always that $|\underline{z}| > \sqrt{2}$

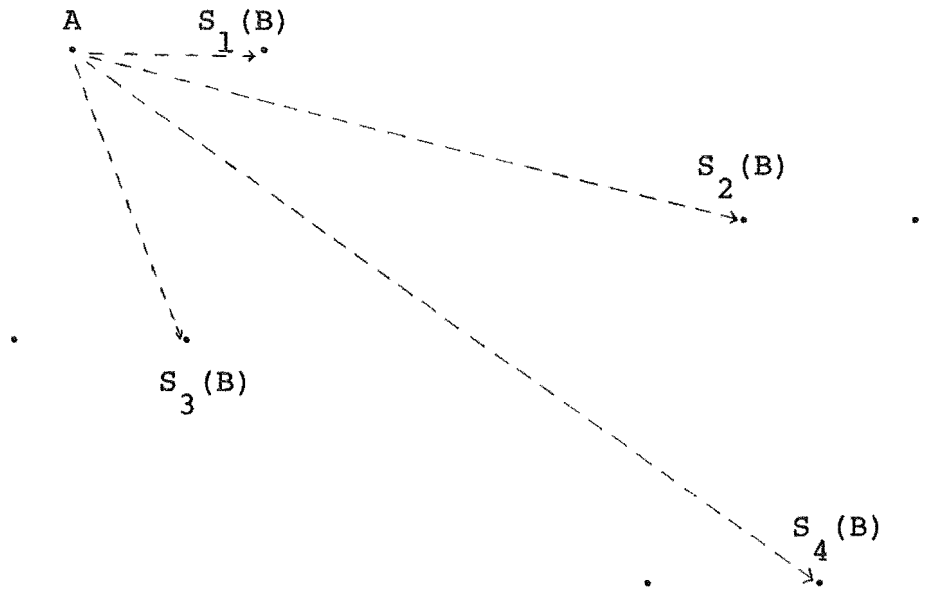
Having thus obtained a set {A} of n(A) possible atomic positions, each of which has eight possible representations, it is necessary to find the set (or sets) of such positions, which show the greatest consistency with the Patterson map vectors.

The set {A} is expanded to contain the 8n(A) possible vectors and contracted partially, where possible, by the elimination of those which are related by the space group symmetry to obtain the set A'. Differences are then taken between members of the set and individually compared with the set of vectors which comprise the Patterson map.

Consider an atom at A and another at B, then vectors A-> S(B) are formed, where S represents the operation on B of the space group symmetry operations. (S_1 is the identity operation so $S_1(B) = B$). For atoms A and B, a maximum of N vectors may be

Figure 12.1.3

VECTORS IN PATTERSON SPACE



found. The vectors are counted as they are located and a matrix of these counts is printed out. It is symmetric about the diagonal. Examination of the matrix will indicate a set of atomic positions consistent among themselves with the Patterson peaks.

The matrix of Table 12.1.3a shows such a set. There are three distinct sets of positions each with two unique possibilities.

Table 12.1.3a

VECTOR COUNT MATRIX

	x'_1	x''_1	x'_2	x''_2	x'_3	x''_3
x'_1	4	4	2	2	4	3
x''_1	4	<u>4</u>	2	<u>4</u>	<u>3</u>	0
x'_2	2	2	2	3	4	4
x''_2	2	<u>4</u>	3	<u>4</u>	<u>4</u>	4
x'_3	4	<u>3</u>	4	<u>4</u>	<u>4</u>	4
x''_3	3	0	4	4	4	2

The set of positions showing greatest consistency are underlined and the submatrix obtained is presented in Table 12.1.3b.

Table 12.1.3b

VECTOR COUNT SUBMATRIX

4	4	3
4	4	4
3	4	4

The positions are x''_1, x''_2, and x'_3. It is possible for more than one such set to be found and the two are frequently related by a translation. This may or may not be between equivalent origins. If so any one will do, if not each model position can be tested.

12.1.4 VERIFICATION OF MODEL'S CONSISTENCY WITH THE PATTERSON MAP

This falls into two modes. The first, tests consistency of new atom positions, with those already established. A rectangular matrix is produced, with all atom positions listed downwards and the known atom positions listed across. Table 12.1.4a shows the

Table 12.1.4a

POSITIONAL CONSISTENCY MATRIX

	x_1	x_2	x_3
x_1	4	4	4
x_2	4	4	3
x_3	4	3	2
a_1	4	4	1
a_2	4	2	4
a_3	0	2	1
a_4	4	4	2

case for three established positions and four proposed positions of which a_3 is clearly incorrect whilst a_1, a_2, and a_4 are likely to be correct.

The second mode is that in which the established and new positions are all checked against each other. An example is given as Table 12.1.4b.

Table 12.1.4b

MATRIX OF ESTABLISHED AND NEW POSITIONS

	x_1	x_2	x_3	b_1	b_2	b_3	b_4
x_1	4	4	3	3	2	1	0
x_2	4	4	2	3	4	0	1
x_3	3	2	4	4	3	1	2
b_1	3	3	4	2	4	0	1
b_2	2	4	3	4	3	2	2
b_3	1	0	1	0	2	4	4
b_4	0	1	2	1	2	4	4

The positions x_1, x_2, x_3, b_1, b_2 form plenty of Patterson vectors as do b_3 and b_4. It is possible that by an allowed translation b_3 and b_4 could be brought into better positions with respect to the first five positions.

12.1.5 MODEL EXTENSION BY ATOMIC SUPERPOSITION

As the Patterson map contains N copies of the chemical structure, each of which has an atom at the origin of the map, the addition of an atomic position vector to the peak positions will move one such structure to the correct chemical site. Those Patterson peaks which show good agreement with the Patterson map when vectors are formed between them and several atomic positions, already found, may yield further atomic positions. Each of the atomic sites known at any point in time may be used for the Patterson map translation, as some may enable better resolution of 'molecular fragments' than others. The usual geometrical tests should be made for chemical sense. This process is one of atomic superposition, and, as it only uses the peak positions, it could be expected to be lighter in its use of computing resources, than those using all calculated points in vector space. As more atomic positions are found they are added in, and assist in the location of further atomic sites.

The program, when running under this option, uses the processes described in Task 2, and some empirically determined criteria, to indicate likely atomic positions, amongst those which are possibilities.

12.2 LINEPRINTER SHADED ELECTRON DENSITY MAPS (ARTSTC)

12.2.1 INTRODUCTION

A major task in crystallography is the computer simulation of the contents of the unit cell of the crystal concerned, and visual representations of the electron density can be a useful aid to structure solution. The unit cell is, in general, a parallelepiped defined by the vectors $\underline{a},\underline{b},\underline{c}$. The electron density is usually calculated at discrete points in planar sections parallel to a face of the unit cell. The shape of the sections is that of a parallelogram.

This program represents the electron density by a shaded map, in which various characters are produced by overprinting with a

lineprinter. For viewing electron density cross-sections such a representation is superior to alphanumeric (single character) or numeric plots. In the program the electron density is interpolated between the calculated points in order to magnify the printed map. Regions of negative 'electron density' are ignored and the positive values are scaled for purposes of assigning shades to them.

12.2.2 PROGRAM FEATURES

1. Density cross-sections printed for each section.
2. Interpolation for increased clarity, and to minimise topological distortion due to fixed print positions, character height and width, and fixed line spacing.
4. Prints additional copies of all sections on request, and then automatically supplies an overlay grid useful as an aid to reading coordinates.
5. On request prints an overlay grid useful as an aid to reading coordinates.
5. Prints cell dimensions and cm $\mathring{A}$ scale factors.
6. Fractional coordinates are listed for the calculated points.
7. Reproduces cell angles in the range 45° - 135° to within 0.1°.
8. Prints maps of any length, width only being limited by the width of the paper being printed on by the computer.
9. Contours can easily be made by tracing around areas having the same shade.
10. Maximum and minimum density levels can be varied for specific purposes, and this varies the number of shades spread across an interval of the map.
11. The darkest shade in each column of calculated values is printed out at the bottom of each map as an aid to the locating of points of high electron density.
12. The graduated scale of shades is indicated on each map.

12.2.3 PROGRAM CONTROL

User options	By default	User
Range of (electron density)	0 - 1000	$-1000<\rho_{min}<\rho_{max}<1000$
Number of copies	1	1 - 8
Grid	0, 1	9

12.2.4 PROGRAM ALGORITHM

1. Assigns shades to the numbers 1 - 1000.
2. Reads file description.
3. Obtains tangent of section angle as a rational fraction.
4. Calculates normalising factor for electron density.
5. Decides on expansion of map and orientation on page.
6. Begins processing each section by reading electron density values from file.
7. Calculates values for scales.
8. As the rows are read for interpolation a note is kept of regions where $\rho < \rho_{min}$ so that they are not unnecessarily interpolated.
9. Carries out interpolation and places density values in an array so that when the section is printed out row by row the section angle will be reproduced accurately.
10. The values are transferred to a disk file.
11. Cell parameters and map printed out.
12. As each line is assembled the maximum number of overprints for its characters is assessed and the values in each of the calculated columns is also examined, in order in order to find the maximum value.
13. For multiple copies of the maps the printing is repeated.
14. For a grid the program produces a map with dots at the positions of the calculated values.

12.3 SORTLIST

12.3.1 INTRODUCTION

Program SORTLIST was written to replace two programs:- RANGER and FILIST. It has two main functions (a) to carry out a weighting analysis of the reflection data and (b) to produce a table of structure factors in a form suitable for publication or for storage on microfiche.

12.3.2 STATISTICS SECTION

The quantities obtained in the weighting analysis are given in Table 12.3.2a.

Table 12.3.2a

FUNCTIONS CALCULATED IN THE WEIGHTING ANALYSIS

Quantity	Functional form
WSELSQ	$(\Sigma(\|\|F_o\|-\|F_c\|)\|^2/\sigma(F)\|^2)/n$
R factor	$R_1 = (\Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma F_o$
Weighted R factor	$R_2 = [\Sigma(\|\|F_o\|-\|F_c\|\|^2/\sigma(F)^2)/\Sigma(F_o^2/\sigma(F)^2)]^{1/2}$
Average value of F_o	$MNFOBS = (\Sigma F_o)/n$
Error in observation of unit weight.	$ERROR = [\Sigma(\|\|F_o\|-\|F_c\|\|/\sigma(F))^2.N/n(N-m)]^{1/2}$

Where

N = Total number of reflections.
m = Number of variables.
n = Number in class.
$\sigma(F) = \sigma(F^2)/2F_o$
$\sigma(\text{Intensity}) = [c + t_c/t_b(B_1+B_2) + (pI)^2]^{1/2}$
c = counts/second

t_c = count time

t_b = background count time.

B_1 = Background count$_1$

B_2 = Background count$_2$.

I = Intensity.

p = Weighting factor.

Program limits are given in Table 12.3.2b.

Table 12.3.2b.

PROGRAM LIMITS FOR SORTLIST

X	Range(X)	Number of classes	Default Value
$\sin\theta/\lambda$	0 - $(\sin\theta_{max})/\lambda$	30	10
F_o	0 - $F_{o\,max}$	30	10
$\sigma(F)$	0 - σ_{max}	5	5
H	H_{min} - H_{max}	$H_{max} - H_{min} + 1$	Range of varied index =35
K	K_{min} - K_{max}	$K_{max} - K_{min} + 1$	Range of other two
L	L_{min} - L_{max}	$L_{max} - L_{min} + 1$	indices = 45

Other information elucidated by the program is:-

(1) The range of the reflection indices.

(2) The slowest varying index.

(3) The index sorted on.

(4) Those reflections for which $(F_o - F_c)/\sigma(F_o)$.ERROR > 3. That is, those reflections for which agreement is poor.

(5) Duplicate reflections.

(6) A factor to scale p by in order to improve the weighting scheme.

12.3.3 PUBLICATION LISTINGS OF STRUCTURE FACTORS

The table of observed and calculated structure factors is printed out with six columns across a page. A number of columns greater than 6 can be specified and a second portion of that table

is printed. If the table is large it can be split by defining a maximum length for the columns. Normally data are sorted on the slowest varying index, which is the one with smallest integer range. This can be over-ridden and either H, K or L specified. Table 12.3.3 indicates the program characteristics described.

Table 12.3.3

CHARACTERISTICS OF SORTING INDICES

Characteristic	Default	Otherwise
Index sorted on	Slowest varying	H, K or L
Number of columns	11	1 - 12
Number of rows	236	< 400

12.4 BONDSTAT

12.4.1 INTRODUCTION

This program's function is to obtain interatomic bond lengths within a connected chemical unit and to calculate average bond lengths and their standard deviations for specified classes of bonds. The bond lengths listed by the program are all those occurring between specified upper and lower bounds. Within this set those for which the statistics are calculated are indicated by giving a list of characters to search for in specified positions of the atom name. Such a system demands a hierarchical naming system, where the levels of the hierarchy could include atom type, molecule number and bond type. The program is so designed that the ordering of the hierarchy is unimportant, in the naming, as the order desired must be supplied as input. Such a program as this is useful for making comparisons in those cases where several molecules of the same type occur in an asymmetric unit.

12.4.2 PROGRAM DESCRIPTION

The input data, consist of a title, the number of bond types for statistical calculations, the number of identifying characters for the pair of atoms for each bond, bond length bounds, the character position lists, cell constants and the bond character lists. The descriptive part of this information is printed out. Atomic parameter cards are read and atomic coordinates orthogonalised.

Calculations of interatomic distances are made and those lying between the bounds given are printed out. Those atoms for which the characters in the nominated positions in their names coincide with the lists given have bond lengths between themselves and other such atoms included in the statistics calculations. Lastly, for the nominated bond types, the mean bond lengths and standard deviations are printed out.

Details of the necessary input for this program are given in the listing on page 179.

APPENDIX A

STRUCTURE FACTOR TABLES

Observed and Calculated Structure Amplitudes in Electrons for

A 1 PHENANTHRENE PMDA

A 2 FLUORENE PMDA

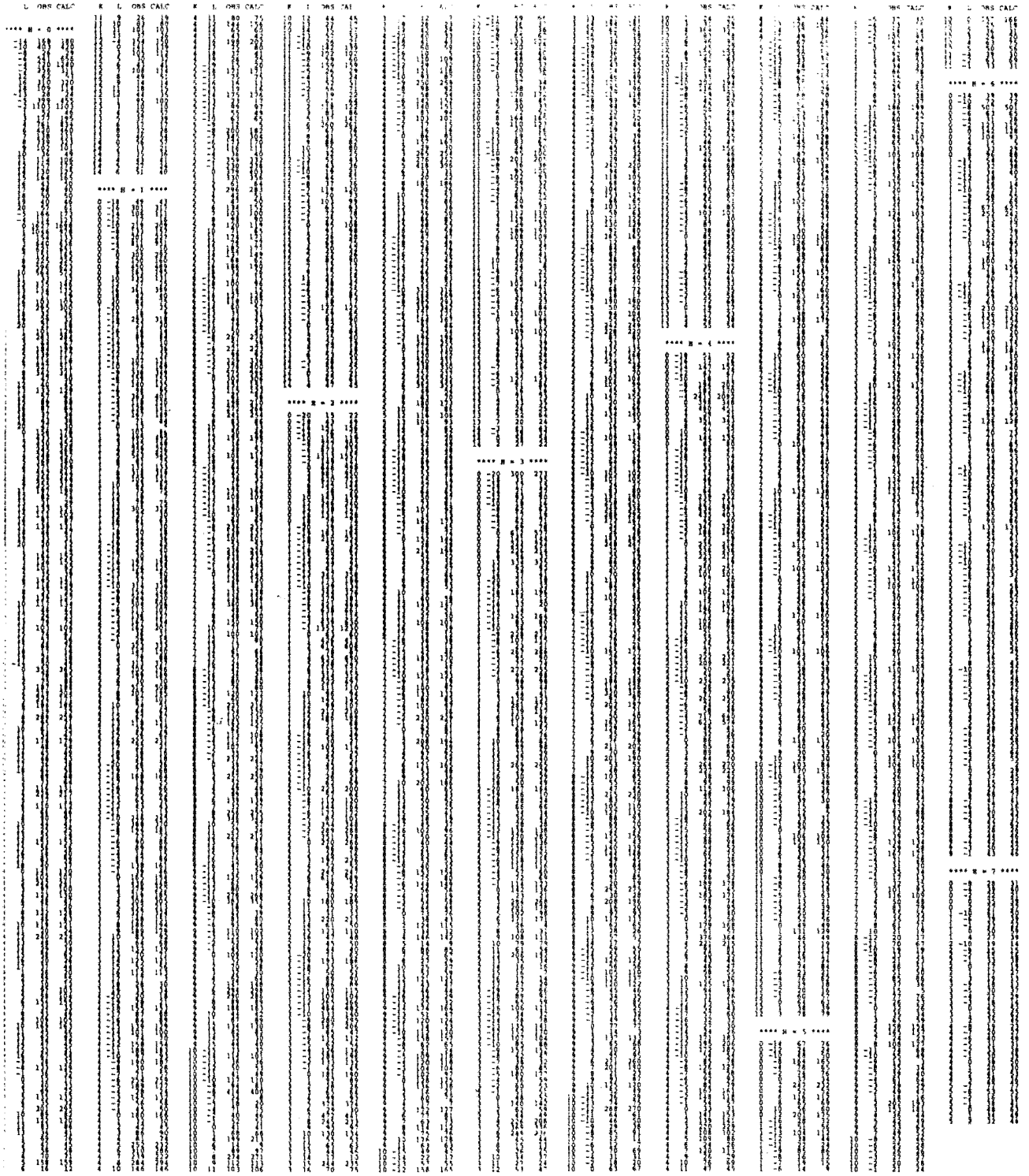
A 3 THIANTHRENE PMDA

A 4 BIPHENYL TNF

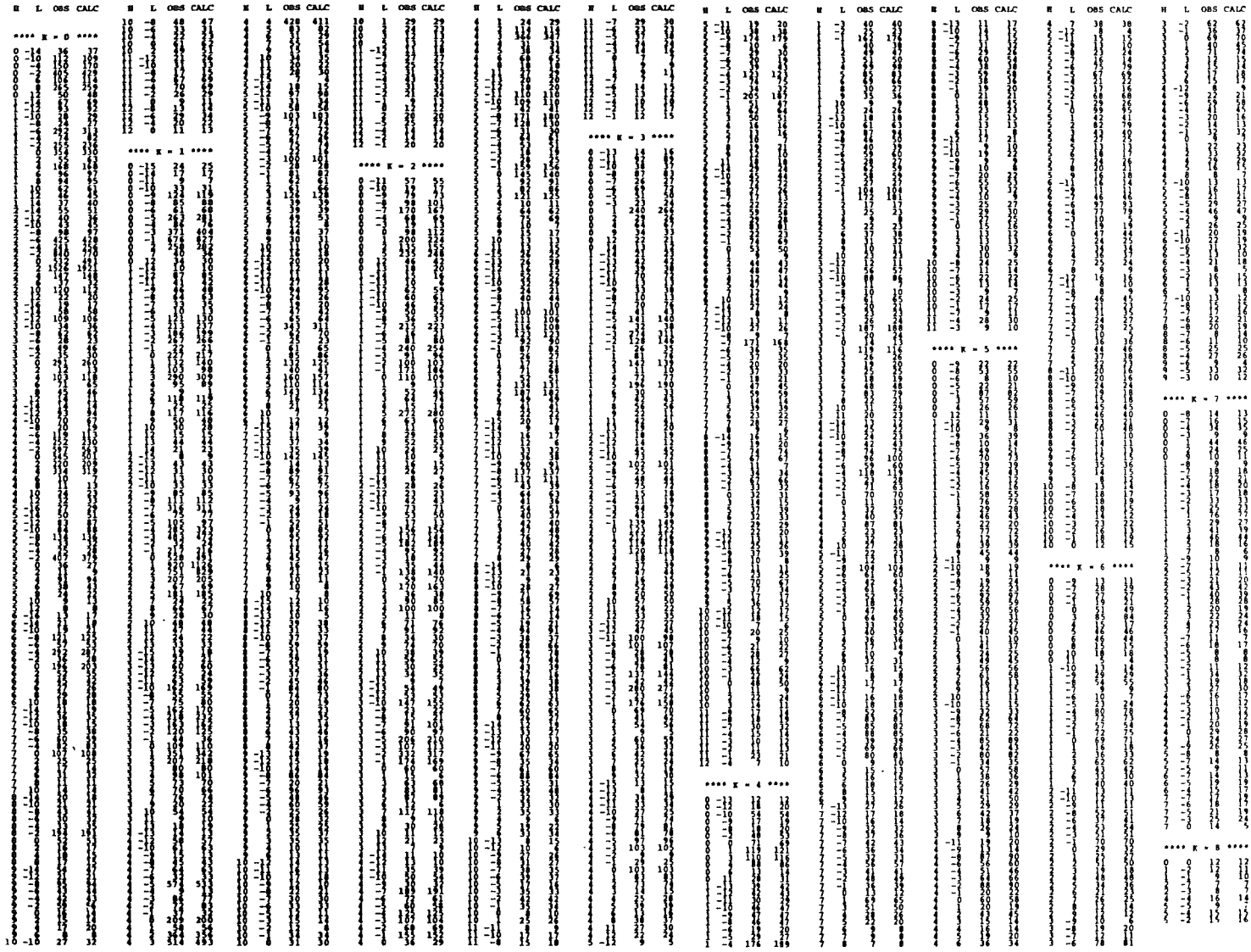
A 5 N-(2-HYDROXYPHENYL) SALICYLALDIMINE DIMETHYL TIN(IV)

A 6 HEXA-μ-DITHIOCACADYLATO TETRAZINCSULPHIDE

PHENANTHRENE PMDA

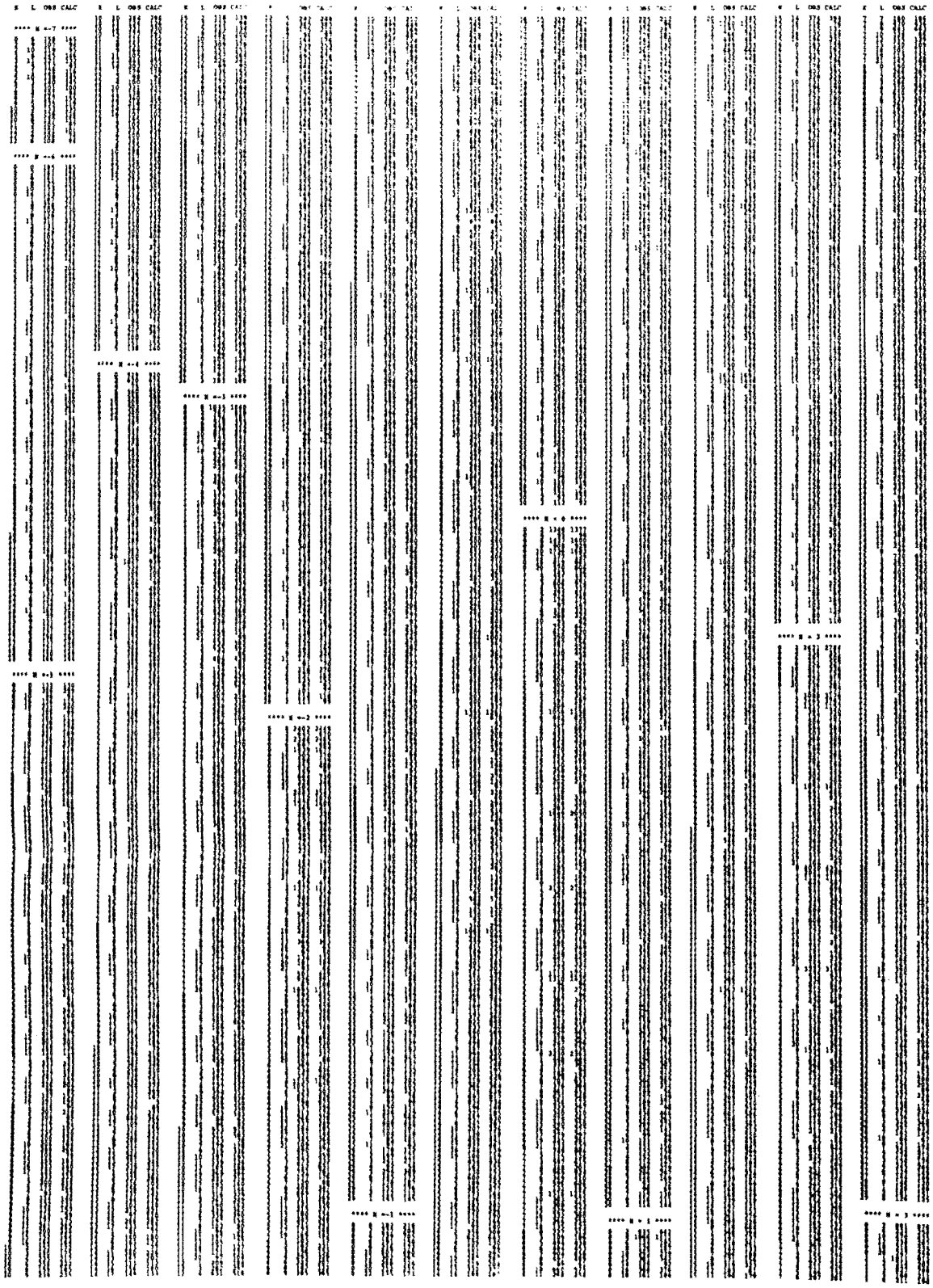


FLUORENE PMDA



THIANTHRENE PMDA

BIPHENYL TRINITROFLUORENONE



BIPHENYL TRINITROFLUORENONE Cont'd

K	L	OBS	CALC
1	7	189	156
1	9	157	157
1	10	164	124
1	11	122	126
1	12	129	112
1	14	325	311
1	17	136	127
1	18	166	179
2	0	215	191
2	1	118	37
2	2	283	299
2	3	452	452
2	4	145	122
2	5	196	200
2	6	253	261
2	7	136	142
2	8	464	429
2	9	284	257
2	10	162	115
2	11	125	114
2	12	148	107
2	16	134	139
2	17	186	193
2	18	174	188
2	19	128	124
2	20	190	196
3	0	250	280
3	1	256	228
3	2	111	298
3	3	205	218
3	5	214	202
3	6	106	104
3	8	379	400
3	10	229	184
3	11	172	86
3	13	118	59
3	15	162	167
3	17	161	148
3	18	193	179
3	19	99	122
4	0	154	188
4	1	243	245
4	2	274	277
4	4	95	49
4	6	181	178
4	7	112	157
4	8	411	365
4	9	558	504
4	10	183	179
4	11	491	488
4	12	195	208
4	14	279	264
4	15	185	210
4	18	175	166
4	19	124	113
5	0	173	340
5	3	122	80
5	4	106	141
5	6	475	479
5	7	161	182
5	9	124	128
5	10	136	91
5	11	262	241
5	12	129	116
5	13	124	116
5	14	174	151
5	15	234	220
5	16	257	279
5	17	309	327
6	0	151	151
6	1	177	149
6	3	401	442
6	5	447	446
6	6	205	217
6	7	339	301
6	8	104	79
6	9	116	82
6	11	103	116
6	12	219	216
6	15	116	170
6	16	206	200
6	19	96	107
7	0	187	190
7	2	326	273
7	3	415	407
7	4	267	253
7	5	255	257
7	9	382	389
7	10	182	207
7	11	162	156
7	12	364	381
7	13	124	104
7	14	313	339
7	15	134	126
7	16	171	179
7	17	298	311
7	18	225	226
7	19	172	182
8	0	317	298
8	2	290	264
8	3	613	603
8	4	440	376
8	6	154	129
8	7	699	658
8	8	293	264
8	9	229	205
8	10	362	340
8	15	291	304
8	17	342	417
8	18	109	116
8	19	132	144
9	0	469	487
9	2	501	499
9	3	98	107
9	4	543	489
9	5	141	124
9	6	356	374
9	7	216	191
9	8	207	229
9	9	137	133
9	10	360	341
9	11	296	297
9	12	109	138
9	13	123	143
9	14	179	189
9	15	119	98
9	16	106	83
9	17	117	100
9	18	141	155
10	0	341	358
10	1	313	311
10	2	233	248
10	3	153	173
10	4	249	204
10	5	193	156
10	6	282	291
10	7	131	181
10	8	221	249
10	12	111	119
10	13	168	190
10	15	271	286
10	16	191	247
10	18	302	340
11	0	127	92
11	1	106	21
11	2	247	231
11	3	162	142
11	4	167	164
11	5	324	315
11	6	229	211
11	7	268	234
11	9	300	262
11	10	314	302
11	11	124	123
11	12	114	228
11	15	138	147
11	16	222	258
11	18	105	140
11	19	199	219
12	0	189	198
12	2	392	367
12	3	252	214
12	4	177	162
12	5	104	92
12	6	219	226
12	7	97	79
12	8	150	172
12	9	314	308
12	10	464	464
12	11	460	378
12	13	619	418
12	14	241	113
12	15	416	224
12	16	284	191
12	17	205	46
12	18	432	230
12	19	326	167
13	0	652	333
13	1	505	464
13	2	460	378
13	3	265	331
13	4	241	113
13	5	416	224
13	6	284	191
13	7	205	46
13	8	432	230
13	9	326	167
13	12	652	333
13	16	152	157
13	17	111	136
13	18	140	167
14	1	456	164
14	2	485	193
14	3	275	121
14	4	230	69
14	5	593	202
14	9	288	107
14	10	409	262
14	11	428	345
14	12	360	251
14	14	218	165
14	15	190	201
14	16	175	308
15	1	453	437
15	2	154	133
15	4	174	172
15	7	175	213
15	8	181	122
15	9	244	260
15	10	173	198
15	12	205	207
15	13	249	241
15	15	472	378
16	1	303	197
16	3	245	134
16	4	494	277
16	6	221	97
16	8	259	105
16	9	894	397
16	10	379	136
16	11	277	83
16	15	416	516
17	4	587	191
17	5	479	160
17	6	560	264
17	9	301	157
17	10	445	281
17	12	320	154
17	13	420	156
17	15	244	156
18	0	176	165
18	2	216	224
18	3	171	188
18	4	400	373
18	8	164	206
18	10	243	216
18	11	165	111
18	12	92	65
19	1	257	212
19	3	273	228
19	7	204	255
19	8	219	258
19	12	167	187
20	1	222	247
20	2	403	364
20	4	101	97
20	8	265	331
20	13	115	134
20	14	107	84
21	1	107	138
21	2	113	118
21	4	87	122
21	5	165	242
21	6	114	113
21	11	213	258
22	1	122	191
22	2	151	119
22	4	424	277
22	5	332	424
22	6	167	202
22	8	116	144
22	10	238	260
22	11	98	93
22	12	92	129
23	1	160	122
23	3	143	98
23	6	168	261
23	7	105	84
23	10	119	152
3	12	210	190

**** H = 4 ****

K	L	OBS	CALC
0	2	919	968
0	4	622	595
0	6	340	328
0	8	260	268
0	12	333	333
0	14	154	130
0	16	201	228
0	18	134	152
1	0	492	473
1	1	155	195
1	2	1619	1471
1	3	519	486
1	4	1261	1195
1	6	311	316
1	7	177	157
1	8	174	132
1	9	336	360
1	11	160	141
1	12	208	213
1	14	232	248
1	17	173	177
2	-1	1199	1139
2	0	764	746
2	1	154	143
2	2	709	687
2	3	419	413
2	4	520	504
2	5	330	345
2	6	141	141
2	7	222	231
2	8	97	114
2	9	298	302
2	13	326	368
2	14	172	218
2	17	113	89
3	0	82	68

**** H = 5 ****

K	L	OBS	CALC
3	11	113	147
3	13	331	325
3	14	216	197
3	15	126	63
3	17	173	156
4	0	512	504
4	1	423	379
4	2	119	114
4	3	131	127
4	4	135	106
4	5	242	260
4	6	107	125
4	7	264	271
4	8	370	365
4	11	127	154
4	12	164	161
4	16	154	169
5	0	676	649
5	1	863	873
5	2	126	129
5	3	325	314
5	4	566	585
5	5	275	253
5	9	205	165
5	11	152	117
5	14	222	238
5	15	110	112
5	16	187	207
5	17	294	289
6	0	942	807
6	1	118	114
6	2	128	169
6	3	305	281
6	4	192	196
6	5	257	272
6	6	360	361
6	8	155	129
6	9	209	214
6	10	154	190
6	11	189	150
6	13	150	141
7	0	1064	972
7	1	267	291
7	2	170	155
7	3	141	143
7	4	149	126
7	6	160	153
7	7	162	154
7	8	134	110
7	9	217	212
7	11	140	145
7	13	254	240
7	16	303	340
7	17	196	211
8	0	557	561
8	2	197	193
8	3	144	167
8	6	229	195
8	11	238	223
9	0	345	327
9	1	232	222
9	2	100	350
9	6	132	118
9	7	220	243
9	8	102	102
9	11	125	119

K	L	OBS	CALC
9	13	132	120
9	14	137	161
9	15	99	69
9	16	146	142
9	17	123	122
10	0	245	228
10	1	137	113
10	2	242	238
10	7	174	167
10	9	118	83
10	10	137	155
10	12	122	110
10	13	143	133
10	14	162	165
10	17	111	123
11	0	339	329
11	1	144	141
11	5	307	326
11	11	132	196
12	1	91	92
12	2	151	160
12	4	91	78
12	7	99	104
12	10	121	142
12	11	122	138
12	16	120	108
13	2	250	242
13	3	154	170
13	4	100	92
13	5	360	384
13	8	182	165
13	9	212	246
13	11	129	149
14	0	148	151
14	1	352	310
14	5	133	73
14	6	124	130
14	7	176	188
14	11	155	179
14	12	146	142
14	13	169	202
15	0	84	62
15	1	102	224
15	2	149	126
15	3	330	324
15	4	157	178
15	5	380	388
15	6	272	331
15	7	174	173
15	8	279	270
15	9	118	108
15	11	157	171
15	14	96	85
16	0	177	185
16	1	161	184
16	2	177	180
16	5	129	157
16	12	110	144
16	14	94	113
17	2	211	243
17	4	220	218
17	8	151	173
17	9	184	220
17	10	100	103
17	14	143	188

K	L	OBS	CALC
18	0	174	166
18	1	113	142
18	4	243	280
18	6	267	297
18	8	114	171
18	10	204	214
18	11	213	261
18	12	115	139
19	0	289	331
19	5	117	123
19	8	200	215
20	1	126	113
20	7	112	116
20	10	119	162
20	11	94	65
21	1	149	190
21	2	167	206
21	3	102	72
21	4	150	140
21	8	104	141
21	10	143	148
22	0	279	291
22	1	175	195
22	2	202	192
22	3	202	195
22	4	156	166
22	5	217	263
22	6	102	99
22	9	108	136
23	1	192	202
23	3	134	145
23	5	132	192
23	6	101	107
24	0	308	364
24	1	128	158
24	5	193	196
24	7	211	227
25	0	131	125
25	5	135	184
26	0	160	185
26	1	174	214
26	2	131	157

**** H = 6 ****

K	L	OBS	CALC
0	4	418	370
0	6	172	172
0	8	330	323
1	0	115	118
1	4	241	269
1	5	108	111
1	9	198	189
1	16	123	141
2	1	194	191
2	2	177	180
2	5	129	157
2	6	268	267
2	7	212	215
2	16	128	159
3	0	148	175
3	1	181	224
3	2	212	233
3	5	185	204
3	10	142	142

K	L	OBS	CALC
3	16	106	89
4	0	420	437
4	4	128	122
4	8	108	122
4	10	174	212
4	11	172	215
4	12	107	141
4	15	225	247
5	0	162	143
5	1	191	219
5	2	217	183
5	3	160	192
5	4	174	213
5	5	118	119
5	8	103	141
5	10	174	191
5	11	144	164
5	12	160	201
6	0	185	191
6	1	225	240
6	9	110	117
6	11	109	109
7	0	128	109
7	1	99	87
7	4	98	74
7	5	122	113
7	11	231	281
7	12	205	229
7	14	117	113
8	0	177	199
8	1	103	82
8	2	197	211
8	3	141	192
8	4	117	121
8	11	118	111
8	15	219	245
9	3	145	179
9	5	112	96
9	8	151	121
9	9	200	269
9	15	89	80
10	0	113	110
10	1	113	101
10	2	134	150
10	3	181	127
10	8	130	164
10	9	116	127
10	10	115	153
10	11	215	290
10	13	141	132
10	14	110	123
11	0	241	264
11	1	176	181
11	2	217	254
11	3	111	124
11	6	131	117
11	8	162	173
11	9	268	267
12	1	243	276
12	2	136	101
12	3	242	229
12	9	225	229
12	10	114	140
13	0	100	102
13	1	140	111
13	7	278	121

**** H = 7 ****

K	L	OBS	CALC
0	2	451	442
0	4	1456	871
0	6	454	464
0	8	624	280
0	12	163	197
1	5	241	195
1	6	419	201
1	8	249	138
2	0	105	147
2	2	219	219
2	4	610	670
2	5	515	565
2	9	106	81
2	10	109	113
3	0	110	108
3	2	124	170
3	5	124	174
3	11	105	117
4	2	196	211

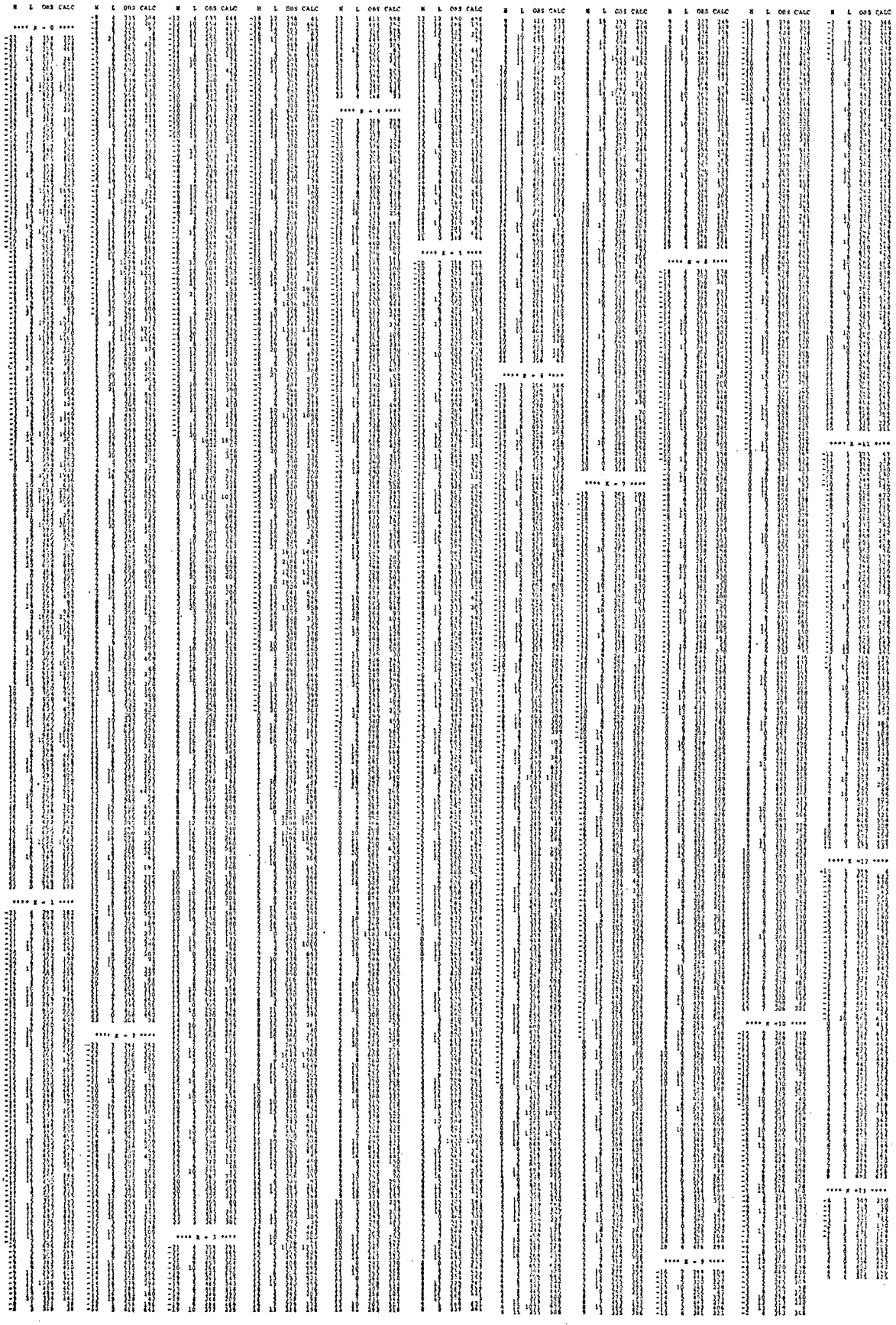
K	L	OBS	CALC
4	1	231	214
4	4	182	205
4	5	104	109
4	10	327	348
4	11	340	370
5	4	127	124
5	6	255	278
5	12	105	99
6	0	108	88
6	1	252	270
6	5	211	192
6	6	136	190
7	7	118	117
7	11	154	146
7	13	161	137
8	1	104	93
8	10	150	171
8	11	106	122
8	12	102	126
9	6	102	106
9	7	122	168
9	8	115	115
9	9	118	118

**** H = 8 ****

K	L	OBS	CALC
1	6	111	176
1	7	111	110
1	8	106	113
1	9	128	101
2	1	136	111
2	2	106	111
2	3	172	122
3	1	100	97
3	2	109	147
3	4	172	120

N-(2-HYDROXYPHENYL) SALICYLALDIMINE DIMETHYL TIN(IV)

HEXA-μ-DITHIOCACADYLATO TETRAZINCSULPHIDE



APPENDIX B.

SCALING OF INTENSITY DATA.

It is normal practice to scale data, thus accounting for variations in reflection intensity during data collection. A few primary standard reflections, collected at regular intervals during data collection are used for this purpose. If absorption corrections are required, they can be applied using either numerical or analytical computing techniques. The use of only a few standards can be quite a crude method of correction of other intensities which are well removed from them in reciprocal space. Variations can also be detected and corrected using, as secondary standards, those classes of reflections, in which corresponding members must, by symmetry be of equal intensity. When for instance it is legitimate to average the reflections hk0 and $\bar{h}$k0, then it is common practice to do so.

Scaling of the general hkl reflections should be carried out in a similar way in order to be consistent.
The quantity

$$I(hk0) = I_o(hk0)\ (1 + \frac{I_o(\bar{h}k0)}{I_o(hk0)})^{\frac{1}{2}} = I_o(hk0)s_{hk}$$

is the average of I(hk0) and I($\bar{h}$k0) and defines a scale factor s_{hk}. The scale factor s_{hk+1} is defined in the same way. What of the intervening reflections ? If s_{hk} were to equal s_{hk+1} it would seem reasonable to scale them by s_{hk} also. For s_{hk} and s_{hk+1} differing it is not an unreasonable first approximation to assume that any variation between them is linear. Such linear variation in scaling factors is introduced in the expression

$$I(hkl) = I_o(hkl)(s_{hk}\ f_l + s_{hk+1}\ (1 - f_l))$$

where f_l is the fraction $1/n(l)$, $n(l)$ being the number of reflections observed from planes between (hk0) and (h k+1 0).

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C      ************************************************************
CC    PROGRAM *PATINV* IS USED TO INVESTIGATE THE PEAKS OF A PATTERSON
CC    MAP.
C      ************************************************************
CC     FUNCTIONS
CC    WITH THE VECTORS IN THE PATTERSON MAP
CC     CHECKING A PROPOSED STRUCTURE TO SEE WHICH ATOMS ARE CONSISTENT
CC     EXTENSION OF THE LIST OF PATTERSON MAP PEAKS
CC     SOLUTION OF PATTERSON MAP GIVEN 3 KNOWN ATOMIC POSITIONS (E.G.
CC     SITES DETERMINED FROM HARKER PEAKS)
CC
CC     ******STRATEGY******
CC      THE LARGER THE LIST OF PATTERSON PEAKS IS THE MORE FRUITFUL IS
CC     THE USE OF THIS PROGRAM
CC (1) FIND ATOM POSITIONS FROM HARKER PEAKS. TEST THESE FOR INTERNAL
CC     CONSISTENCY USE SELFCN=1
CC  (2) TEST PROPOSED STRUCTURE USING KNOWN PEAKS TO FORM VECTORS
CC  (3) TEST PROPOSED STRUCTURE AGAINST ITSELF AS IN (1) I.E. SELFCN=1
CC (4) TRY SOLVE
CC (5) USE OF KNPKXN,PATPXN MAY HELP
CC
CC     OPERATING INSTRUCTIONS
CC   NSYM              NO. OF SYMETTRY CARDS FOR SPACE GROUP - ALL REQUIRED
CC   NOPTPK            NO. OF PATTERSON PEAKS
CC    NKNAT            NO. OF KNOWN POSITIONS
CC    NOPK             NUMBER OF POSITIONS IN PROPOSED STRUCTURE
CC   TOLNC             3 TOLERANCE VALUES REQUIRED
CC                   SUGGEST 0.4/A, 0.4,B, 0.4/C
CC   PATEXN     0      NO EXTENSION OF PATTERSON PEAK LIST
CC              1      EXTENSIN OF PATTERSON PEAK LIST
CC              1      EXTEND LIST OF 'KNOWN' PEAKS
CC   ALLPAT     0 NO ACTION
CC              1 TREATS PATTERSON PEAKS AS PROPOSED STRUCTURE
CC                   NKNAT,NOPK MUST BE SET EQUAL TO NOPTPK
CC   SELFCN     0 TESTS NOPK PEAKS AGAINST NKNAT KNOWN ATOMS FOR
CC                   CONSISTENCY WITH PATTERSON
CC              1 TESTS A PROPOSED STRUCTURE FOR SELF CONSISTENCY
CC                   SET NOPK = NKNAT
CC   SOLVE      0      NO ACTION
CC              1      SUBTRACTS A SUCCESSION OF PEAKS FROM  ALL PATTERSON
CC                     PEAKS AND MAKES VECTORS FROM THE NEW PEAKS AND THE
CC                      (SUGGEST
CC                      3) KNOWN POSITIONS AND TESTS WITH THE  PATTERSON
CC                     PEAKS FOR CONSISTENCY
CC              2 AS ALLPAT=1 PLUS AS FOR SOLVE =1 AND GIVES SUGGESTED
CC                     ATOM POSITIONS
CC                     IF SOLVE IS SET TO 2 SET NKNAT,NOPK=NOPTPK
CC   KNONUM     0 NO ACTION
CC              N      NUMBER OF KNOWN PEAKS - ONLY SET WHEN SOLVE=2
CC   **FORMAT** 4I5,3F5.4,6I5
CC C2                  THE NSYM SYMMETRY CARDS OF THE SPACE GROUP
CC  **FORMAT**  AS FOR CUCLS
CC  C3                 THE NOPTPK PATTERSON PEAKS
CC  **FORMAT** 3F10.8
CC C4                  THE NKNAT KNOWN ATOM POSITIONS
CC  **FORMAT**3F10.8
CC                     IF ALLPAT =1 OMIT
CC C5                  POSITIONS OF ATOMS IN PROPOSED STRUCTURE
CC  **FORMAT**         3F10.8
CC                     IF ALLPAT=1 OMIT
CC                     IF SELFCN=1 OMIT
CC                     IF KNPKXN=1 OMIT
CC                     IF SOLVE=1 OMIT
CC                     IF SOLVE=2 OMIT
      DIMENSION HARKER(30,6),HARKTP(30,3),ACCPRS(50,2),WPEAK(1500,4)
      DIMENSION IND(6),MUMP(25)
      DIMENSION NUMP(3),TYPE(25,5),KNUM(100),TYPOLP(24)
      DIMENSION X(200,3)
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```
      DIMENSION CHECK1(100),CHECK2(100),CHECK3(100),APEAK(100,3)
      DIMENSION RATING(100)
      DIMENSION PEAK(6000,3),DIFPK(2000,3),FREPTP(1000),NUMPK(1000)
      DIMENSION TOLNC(3)
      DIMENSION NUMSPK(80,80)
      DIMENSION SPEAK(6000,3)
      DIMENSION PPEAK(1000,3),FPEAK(300,3),JHALF(7,3)
      DIMENSION SYMRL(8,6),SYMPAT(8,6),PATPK(1000,3),KNATOM(300,3)
       DIMENSION JMA(3),MAP(51,51,24),AMULT(3)
      DIMENSION SYM(10)
      DATA AMULT/44.0,32.0,46.0/
      INTEGER PK,SELFCN,ALLPAT,PATEXN
      INTEGER SOLVE
      INTEGER TYPE,HARKTP
      INTEGER D
      INTEGER PAT
      REAL KNATOM
      DATA IND/2,2,4,4,6,6/
      INTEGER MAPS
      DATA JHALF/1,0,0,1,1,0,1,
     *0,1,0,1,0,1,1,
     *0,0,1,0,1,1,1/
   50 FORMAT(4I5,3F5.4,9I5)
   60 FORMAT(1X,'NSYM=',I2,'NOPTPK=',I3,'NKNAT=',I3,'NOPK=',I3,'TOLNCS',
     *3F5.4,'PATEXN=',I2,'KNPKXN=',I2,'ALLPAT=',I2,'SELFCN='I2,'SOLVE=',
     *I2,'KNONUM= ',I2,'HARK= ',I2,'PATSYM= ',I2)
  100 FORMAT(30X,3F10.6)
  303 FORMAT(30X,3F10.6)
  304 FORMAT(F15.8,I3,7X,F14.8,3X,I3,3X,F15.8,6X,I3)
  306 FORMAT(30X,3F10.8)
  200 FORMAT(1X,3F10.4,5X,I3)
  203 FORMAT(1X,3F10.4,5X,I3,2X,*A1)
  205 FORMAT(1X,'PATTERSON PEAKS',14X,'FREQUENCY')
  206 FORMAT(1X,'PEAKS',24X,'NUMBER')
  400 FORMAT(1X,F5.2,2X,I2,'X',2X,F5.2,2X,I2,'Y',2X,F5.2,2X,I2,'Z',
     *       2X,F5.2,2X,I2,'X',2X,F5.2,2X,I2,'Y',2X,F5.2,2X,I2,'Z')
  803 FORMAT(1X,'NEW PEAKS FOUND, FROM PAT. PEAK NO., NO KNOWN ATOMS,
     *AGREEMENT LEVEL')
  801 FORMAT(1X,3F10.6,3(5X,I5))
  903 FORMAT(1X,'HARKER VECTORS')
 8008 FORMAT(1X,'ACCEPTED PEAKS',17X,'RATING')
 8007 FORMAT(1X,3F10.8,I6)
 1000 FORMAT(1X,' ')
40003 FORMAT(1X,2I5)
      PSYMR=1
      ESTAT=10
      DIMENSION TITLE(14)
      READ(5,98642)TITLE
98642 FORMAT(13A6,A2)
      WRITE(6,98643)TITLE
98643 FORMAT(21X,13A6,A2)
      READ(5,7821)SYM
 7821 FORMAT(9A1)
      SYM(10)='*'
      READ(5,50) NSYM,NOPTPK,NKNAT,NOPK,(TOLNC(JV),JV=1,3),PATEXN,
     *KNPKXN,ALLPAT,SELFCN,SOLVE,KNONUM,HARK,PATSYM,NREMOV
      READ(5,50003) MAPS,KUMP,ICENT
50003 FORMAT(3I5)
      IF (SOLVE.EQ.2) ALLPAT=1
      IF(ALLPAT.EQ.1) SELFCN=1
      IF(ALLPAT.EQ.1) PSYMR=0
      WRITE(6,60) NSYM,NOPTPK,NKNAT,NOPK,(TOLNC(JV),JV=1,3),PATEXN,
     *KNPKXN,ALLPAT,SELFCN,SOLVE,KNONUM,HARK,PATSYM
      NNKNAT=NKNAT
C
CC***** READ IN SYM CARDS
C
      WRITE(6,399)
```

```
  399 FORMAT(1X,'SPACE GROUP SYMMETRY',20X,'PATTERSON SYMMETRY')
      DO 103 JS = 1,NSYM
      READ (5,304)(SYMRL(JS,N),N=1,6)
C
CC***** CREATE PATTERSON SYM
C
      DO 104 JSP=2,6,2
      SYMPAT(JS,JSP)=SYMRL(JS,JSP)
  104 CONTINUE
  103 CONTINUE
      IF(ICENT.GT.0) PAT=1
      DO 1103 JS=1,NSYM*SYM(1+PAT)
      IF(PATSYM.EQ.0) GO TO 11113
      READ(5,304)(SYMPAT(JS,N),N=1,6)
11113 CONTINUE
      WRITE(6,400)(SYMRL(JS,N),N=1,6),(SYMPAT(JS,JSP),JSP=1,6)
 1103 CONTINUE
C
CC***** READ IN PATTERSON PEAKS
C
      IF(ALLPAT.EQ.1) GO TO 1102
      DO 102 JJ = 1,NOPTPK
      READ(5,303)(PATPK(JJ,M),M=1,3)
  102 CONTINUE
 1102 CONTINUE
        IF(HARK.EQ.1) GO TO 9002
      GO TO 9004
 9002 CONTINUE
C
CC***** CREATE HARKER GEOMETRIES FROM SYMMETRY ELEMENTS OF SPACE GROUP
C
      WRITE(6,903)
      DO 900 JP=1,NSYM-1
      DO 901 JPP=JP+1,NSYM
      JHR=JHR+1
      DO 902 JRR=1,6
      HARKER(JHR,JRR)=SYMRL(JP,JRR)-SYMRL(JPP,JRR)
  902 CONTINUE
      IF(JHR.EQ.1) GO TO 899
      DO 9902 JW=1,JHR-1
      DO 9903 JV=1,NSYM*SYM(1+PAT)
      IPN =0
      DO 9904 JTV=1,6
      IF(AMOD(ABS(HARKER(JHR,JTV)-HARKER(JW,JTV)*SYMPAT(JV,IND(JTV))
     *)+0.001,10**(AMOD(JTV+1,2))).LT.0.002) IPN=IPN+1
 9904 CONTINUE
      IF(IPN.NE.6) GO TO 9903
      JHR=JHR-1
      GO TO 901
 9903 CONTINUE
 9902 CONTINUE
  899 CONTINUE
      WRITE(6,400) (HARKER(JHR,JRS),JRS=1,6)
  901 CONTINUE
  900 CONTINUE
      NOHKTP=JHR
      WRITE(6,7002)
 7002 FORMAT(1X,'HARKER TYPES')
C
CC***** CHECK HARKER GEOMETRIES FOR CONSTANT COORDINATES
C
      DO 906 JHT=1,NOHKTP
      DO 907 JSS=2,6,2
      IF(ABS(HARKER(JHT,JSS)).LT.0.001) GO TO 907
      HARKTP(JHT,JSS/2)=1
  907 CONTINUE
      WRITE(6,7001)(HARKTP(JHT,JSL),JSL=1,3)
 7001 FORMAT(1X,3I5)
```

```
  906 CONTINUE
C
C***** DETERMINES WHICH CLASSES OF PATTERSON VECTORS CAN BE USED TO
C***** OBTAIN POSITIONAL VECTORS
C
      WRITE(6,7003)
 7003 FORMAT(1X,'ACCEPTABLE TYPES')
      JCO=NOHKTP
      NMP=1
      DO 984 IRT=1,JCO-1
      DO 9997 JRZ=1,3
      MUMP(JRZ)=0
 9997 CONTINUE
      NUM=0
      DO 981 JRT=1,3
      IF(HARKTP(IRT,JRT).NE.1) GO TO 981
      MUMP(JRT)=1
      NUM=NUM+1
      IF(NUM.NE.3) GO TO 981
      TYPE(NMP,1) = IRT
      TYPE(NMP,5) = 1
      WRITE(6,986) TYPE(NMP,1)
  986 FORMAT(1X,I5)
      NMP=NMP+1
      GO TO 984
  981 CONTINUE
      N=2
      DO 983 KRT=IRT+1,JCO
      MUM=NUM
      TYPE(NMP,1)=IRT
      TYPE(NMP,N)=KRT
      DO 982 JJRT=1,3
      NUMP(JJRT)=MUMP(JJRT)
      IF(HARKTP(KRT,JJRT).NE.1) GO TO 982
      IF(NUMP(JJRT).NE.1) GO TO 988
      TYPOLP(NMP)=JJRT
      GO TO 982
  988 CONTINUE
      NUMP(JJRT)=1
      MUM=MUM+1
      IF(MUM.NE.3) GO TO 982
      WRITE(6,985) N,(TYPE(NMP,JRL),JRL=1,N) ,TYPOLP(NMP),NMP
  985 FORMAT(1X,*I5,2I5)
      TYPE(NMP, 5) =N
  982 CONTINUE
      NMP=NMP+1
  983 CONTINUE
  984 CONTINUE
      NOATYP=NMP-1
C
C***** FROM PATTERSON PEAKS OBTAIN VALUES FOR VARIABLE COORDINATES OF
C***** THOSE VECTORS WHICH HAVE AT LEAST ONE COORDINATE CONSTANT
C
      DO 908 JIP=1,NOHKTP
      KNUM(JIP) = PX+1
      JN=0
      DO 909 JSS=1,3
      IF(HARKTP(JIP,JSS).EQ.0) JN=JN+1
  909 CONTINUE
      DO 920 JIZ=1,NOPTPK-NREMOV
      L=0
      PX=PX+1
      DO 945 JSR=1,3
      X(PX,JSR)=0.0
      IF(HARKTP(JIP,JSR).EQ.1) GO TO 946
      IF(AMOD(ABS(HARKER(JIP,2*JSR-1)-PATPK(JIZ,JSR))+0.001,1).GT.0.002)
     *GO TO 948
      L=L+1
```

```
      GO TO 945
  946 CONTINUE
      IF(HARKER(JIP,2*JSR).EQ.0) GO TO 935
      X(PX,JSR)=(PATPK(JIZ,JSR)-HARKER(JIP,2*JSR-1))/HARKER(JIP,2*JSR)
  935 CONTINUE
  945 CONTINUE
      IF(L.EQ.JN) WRITE(6,911)(X(PX,JSR),JSR=1,3),(HARKTP(JIP,JIM),JIM=1
     *,3),L,PX,JIP,JIZ,(PATPK(JIZ,JLA),JLA=1,3)
  911 FORMAT(1X,3F10.7,10X,3I5,4I5,3F10.6)
      GO TO 920
  948 PX=PX-1
  920 CONTINUE
  908 CONTINUE
      KNUM(NOHKTP+1)=PX+1
      WRITE(6,20001) NOHKTP,(KNUM(JAB),JAB=1,NOHKTP)
20001 FORMAT(1X,*I5)
      MOP=0
      DO 990 JLP=1,NOATYP
      DO 9993   I=1,3
      IF(HARKTP(TYPE(JLP,1),I).EQ.0) IT=I
 9993 CONTINUE
      DO 994 MO=KNUM(TYPE(JLP,1)),KNUM(TYPE(JLP,1)+1)-1
      IF(TYPE(JLP,5).NE.1) GO TO 99000
      MOP=MOP+1
      DO 99002 J=1,3
      WPEAK(MOP,J)=X(MO,J)
99002 CONTINUE
      WPEAK(MOP,4)=JLP
      WRITE(6,99004)(WPEAK(MOP,JQ),JQ=1,4)
99004 FORMAT(1X,4F10.4)
99000 CONTINUE
      IF(TYPE(JLP,5).NE.2) GO TO 9995
      DO 995 JI=KNUM(TYPE(JLP,2)),KNUM(TYPE(JLP,2)+1)-1
      IF(TYPOLP(JLP) .EQ.0) GO TO 99600
      DO 996 JZ=1,NSYM
      IF(AMOD(ABS(X(MO,TYPOLP(JLP))-X(JI,TYPOLP(JLP))*SYMRL(JZ,2*TYPOLP(
     *JLP))+SYMRL(JZ,2*TYPOLP(JLP)-1))+TOLNC(TYPOLP(JLP)),1).GT.2*TOLNC
     *(TYPOLP(JLP))) GO TO 996
      MOP=MOP+1
      DO 993 I=1,3
      IF(HARKTP(TYPE(JLP,1),I).EQ.0) GO TO 993
      WPEAK(MOP,I)=X(MO,I)
      WPEAK(MOP,4)=JLP
  993 CONTINUE
      WPEAK(MOP,IT)=X(JI,IT)*SYMRL(JZ,2*IT)+SYMRL(JZ,2*IT-1)
      WRITE(6,30000) (WPEAK(MOP,L),L=1,3),MOP,MO,JI,TYPOLP(JLP),IT
30000 FORMAT(1X,3F10.4,5I5)
      GO TO 995
  996 CONTINUE
      GO TO 995
99600 CONTINUE
      MOP = MOP+1
      DO 99601 JQR=1,3
      WPEAK(MOP,JQR)=X(MO,JQR)+X(JI,JQR)
99601 CONTINUE
      WPEAK(MOP,4)=JLP
      WRITE(6,99602)(WPEAK(MOP,JRS),JRS=1,4)
99602 FORMAT(1X,4F10.4)
  995 CONTINUE
 9995 CONTINUE
      IF(TYPE(JLP, 5).NE.3) GO TO 994
      DO 1001 NMO=KNUM(TYPE(JLP,2)),KNUM(TYPE(JLP,2)+1)-1
      MOP=MOP +1
      DO 1002 NRM=1,3
      IF(HARKTP(TYPE(JLP,2),NRM) .EQ.1) WPEAK(MOP,NRM) =X(NMO,NRM)
 1002 CONTINUE
      DO 1003 NMP=KNUM(TYPE(JLP,3)),KNUM(TYPE(JLP,3)+1)-1
      MOP=MOP+1
```

```
      DO 1004 NMM=1,3
      IF(HARKTP(TYPE(JLP,3),NNM).EQ.1) WPEAK(MOP,NMM)=X(NMP,NMM)
 1004 CONTINUE
      WPEAK(MOP,4)=JLP
      WRITE(6,1005) (WPEAK(MOP,NJ),NJ=1,3)
 1005 FORMAT(1X,3F10.4)
 1003 CONTINUE
 1001 CONTINUE
  994 CONTINUE
  990 CONTINUE
      DO 1010 NA=1,MOP-1
      DO 1011 NB=NA+1,MOP
      DO 1012 NC=1,NSYM
       NOND=0
      DO 1013 ND=1,3
      IF(AMOD(2*ABS(WPEAK(NA,ND)-(WPEAK(NB,ND)*SYMRL(NC,2*ND)+SYMRL
     *(NC,2*ND-1)))+2*TOLNC(ND),1).GT.4*TOLNC(ND)) GO TO 1012
      NOND=NOND+1
 1013 CONTINUE
      IF(WPEAK(NB,4)-WPEAK(NA,4).GT.0.001) NOND=NOND+1
      IF(NOND.NE.4) GO TO 1012
      NMOP=NMOP+1
      DO 1014 NDD=1,3
      IF(NMOP.GT.6000) GO TO 1010
       PEAK(NMOP,NDD)=WPEAK(NA,NDD)
 1014 CONTINUE
 1012 CONTINUE
 1011 CONTINUE
 1010 CONTINUE
      IF(MOP.EQ.0)NMOP=5
      IF(MOP.EQ.0)MOP=5
      IJZ=0
C
C***** OBTAINS LIST OF UNIQUE VECTORS
C
      WRITE(6,40001)
40001 FORMAT(1X,'UNIQUE POSITIONS FROM PATTERSON')
      DO 950 LL=1,NMOP
      DO 951 LM=1,IKZ
      IF(IKZ.GT.124) GO TO 950
      DO 952 PRM=1,NSYM*SYM(1+PAT)
      IJ=0
      DO 953 PRL=1,3
      IF(AMOD(ABS(PEAK(LL,PRL)-PPEAK(LM*8-7,PRL)*SYMPAT(PRM,2*PRL))+TOLN
     *C(PRL),1).LT.2*TOLNC(PRL)) IJ=IJ+1
  953 CONTINUE
      IF(IJ.EQ.3) GO TO 950
  952 CONTINUE
  951 CONTINUE
      IJZ=IJZ+1
      DO 954 IJR=1,3
      PPEAK(IJZ*8-7,IJR)=PEAK(LL,IJR)
  954 CONTINUE
      WRITE(6,960) (PPEAK(IJZ*8-7,IRT),IRT=1,3)
  960 FORMAT(1X,3F10.6)
      IKZ=IJZ
  950 CONTINUE
C
C***** EXPANDS LIST 8FOLD TO ALLOW FOR AMBIGUITY OF 0.5 IN EACH
C     COORDINATE.
C
      DO 961 IO=1,IJZ
      DO 962 IOT=1,7
      IOOT=IO*8+IOT-7
      DO 963 IB=1,3
      PPEAK(IOOT,IB)=PPEAK(IO*8-7,IB)+0.5*JHALF(IOT,IB)
  963 CONTINUE
  962 CONTINUE
```

```
  961 CONTINUE
C
C***** OBTAIN LIST OF UNIQUE VECTORS
C
      WRITE(6,40002)
40002 FORMAT(1X,'UNIQUE VECTORS FOLLOWING 8FOLD EXPANSION')
      INZ=0
      DO 970 KI=1,8*IJZ
      DO 971 KII=1,IMZ
      DO 972 KYM=1,NSYM
      IJN=0
      DO 973 IC=1,3
      IF(AMOD(ABS(PPEAK(KI,IC)-FPEAK(KII,IC)*SYMRL(KYM,2*IC)+SYMRL(KYM,
     *2*IC-1))+TOLNC(IC),1).LT.2*TOLNC(IC)) IJN=IJN+1
  973 CONTINUE
      IF(IJN.EQ.3) GO TO 970
  972 CONTINUE
  971 CONTINUE
      INZ=INZ+1
      IF(INZ.GT.200) GO TO 9000
      DO 974 IJN=1,3
      FPEAK(INZ,IJN)=PPEAK(KI,IJN)
  974 CONTINUE
      WRITE(6,978) (FPEAK(INZ,JOP),JOP=1,3)
  978 FORMAT(1X,3F10.6)
      IMZ=INZ
  970 CONTINUE
 9000 CONTINUE
      DO 980 J=1,INZ
      DO 9981 JJ=1,3
      KNATOM(J,JJ)=FPEAK(J,JJ)
      PEAK(J,JJ)=FPEAK(J,JJ)
 9981 CONTINUE
  980 CONTINUE
      NOPK=INZ
      NKNAT=INZ
      IF(SELFCN.EQ.1) GO TO 3001
      GO TO 10000
 9004 CONTINUE
C
C***** READ IN KNOWN ATOMS
C
      GO TO 6001
 6000 NKNAT=KNONUM
 6001 CONTINUE
      DO 101 J = 1,NKNAT
      READ(5,100) (KNATOM(J,L),L=1,3)
      IF(SELFCN.NE.1) GO TO 101
      IF(PID.EQ.1) GO TO 101
      DO 3000 LL=1,3
      PEAK(J,LL)=KNATOM(J,LL)
      IF(ALLPAT.NE.1) GO TO 3000
      PATPK(J,LL)=KNATOM(J,LL)
      WRITE(6,2000) PATPK(J,LL)
 2000 FORMAT(1X,F10.6)
 3000 CONTINUE
  101 CONTINUE
      IF(SELFCN.EQ.1.OR.ALLPAT.EQ.1) GO TO 3001
C
C***** READ IN SUGGESTED PEAKS
C
      IF(SOLVE.EQ.1) GO TO 3001
      DO 105 JPK=1,NOPK
      READ(5,306)(PEAK(JPK,LP),LP=1,3)
  105 CONTINUE
 3001 CONTINUE
      IF(KNPKXN.EQ.0) GO TO 4001
      NOPK=NOPTPK*NSYM
```

```
      NUMNO1=1
       NUMNO2 =NOPTPK
      DO 604 JP=1,NKNAT
      DO 602 JR=NUMNO1,NUMNO2
      DO 601 JSYM=1,NSYM*SYM(1+PAT)
      DO 600 IZ=1,3
       PEAK((JR-1)*NSYM+JSYM,IZ) = PATPK(JR,IZ)*SYMPAT(JSYM,2*IZ) -
     *KNATOM(JP,IZ)
  600 CONTINUE
  601 CONTINUE
  602 CONTINUE
 4001 CONTINUE
      MKNAT=NKNAT
      NPNAT=NKNAT
       IF(SOLVE.EQ.2.AND.PID.EQ.1) GO TO 5002
      IF(SOLVE.NE.1) GO TO 5000
 5002 CONTINUE
      DO 5604 JP=1,NKNAT
      DO 33 JU=1,80
      DO 34 JJU=1,80
      NUMSPK(JJU,JU)=0
   34 CONTINUE
   33 CONTINUE
      DO 35 KU=1,100
      CHECK1(KU) =0
      CHECK2(KU)=0
      DO 36 KKU=1,3
      APEAK(KU,KKU) = 0
   36 CONTINUE
   35 CONTINUE
      DO 37 KLM=1,1000
      FREPTP(KLM) =0
   37 CONTINUE
      DO 5603 JT=1,NOPTPK
      DO 5061 IT=1,3
      PEAK(JT,IT)=PATPK(JT,IT)-KNATOM(JP,IT)
 5061 CONTINUE
 5603 CONTINUE
 5000 CONTINUE
C
C***** EXPAND PEAK LIST BY GENERATION OF EQUIVALENT PEAKS USING SYM. OPS
C
      DO 109 PK=1,NOPK
      DO 110 ISYM=1,NSYM
      DO 111 IS=1,3
      SPEAK(NSYM*(PK-1)+ISYM,IS)=AMOD(PEAK(PK,IS)*SYMRL(ISYM,2*IS)+PSYMR
     **SYMRL(ISYM,2*IS-1),1)
  111 CONTINUE
  110 CONTINUE
  109 CONTINUE
  500 CONTINUE
C
C*****CALCULATE DIFFERENCE BETWEEN KNOWN ATOM FOR ALL PEAKS IN
C***** EXPANDED PEAKS LIST 1 COMPONENT AT A TIME
C
      DO 106 NJ=1,NPNAT
      NUM=0
      NZUM=0
      DO 108 JZ=1,NOPK*NSYM
      IF(AMOD(JZ,NSYM).EQ.1) NUM=0
      DO 107 I=1,3
      DIFPK(JZ,I)=AMOD(KNATOM(NJ,I)-SPEAK(JZ,I)   ,1)
      JMA(AMOD(I+KUMP-1,3)+1)=AMOD(DIFPK(JZ,I)+1.0,1)*AMULT(AMOD(I+KUMP-
     *1,3)+1)+1.5
  107 CONTINUE
      IF(MAPS.EQ.0) GO TO 11102
      MAP(JMA(1),JMA(2),JMA(3))=MAP(JMA(1),JMA(2),JMA(3))+1
11102 CONTINUE
```

```
C
C***** GO THROUGH THE PATTERSON PEAKS AND ALL THEIR SYM. EQUIVALENTS AND
C***** TEST FOR EQUALITY WITH THE DIFFERENCE VECTORS ABOVE COMPONENT BY
C***** COMPONENT.
C
      DO 113 JY=1,NOPTPK
      DO 112 JSY=1,NSYM*SYM(1+PAT)
      DO 115 IL=1,3
      IF(AMOD(ABS(DIFPK(JZ,IL)-PATPK(JY,IL)*SYMPAT(JSY,2*IL))+TOLNC(IL),
     *1).GT.2*TOLNC(IL)) GO TO 112
C
C***** IF ALL CPTS. OF PATTERSON PEAK OR ITS EQUIVALENT EQUAL TO DIFF.
C***** PEAK ADD 1 TO FREQUENCY OF OCCURRENCE OF PATTERSON PEAK
C
      IF(IL.EQ.3) FREPTP(JY)=FREPTP(JY)+1
      IF (IL.EQ.3) NUM=NUM+1
C
C***** IF ALL 4 SYM. DIFF. ARE LOCATED THE PEAK IS LIKELY TO BE TRUE AND
C***** ADD 1 TO ITS COUNT
C
      IF (NUM.EQ.NSYM) NUMPK((JZ+(NSYM-1))/NSYM)=NUMPK((JZ+(NSYM-1))/NSY
     *M)+1
      IF(IL.EQ.3) GO TO 1108
  115 CONTINUE
  112 CONTINUE
      IF(SOLVE.EQ.2.AND.PID.EQ.0) CHECK3(JY)=NUMPK(JY)
  113 CONTINUE
      IF(PATEXN.EQ.0) GO TO 1108
      DO 4561 JRZ=1,NZUM
      DO 4562 JRW=1,NSYM*SYM(1+PAT)
      DO 4563 JRY=1,3
      IF(AMOD(ABS(DIFPK(JZ,JRY)-PATPK(NOPTPK+JRZ,JRY)*SYMPAT(JRW,2*JRY))
     *+TOLNC(JRY),1).GT.2*TOLNC(JRY)) GO TO 4562
      IF(JRY.EQ.3) FREPTP(NOPTPK+JRZ)=FREPTP(JRZ+NOPTPK)+1
      IF(JRY.EQ.3) GO TO 1108
 4563 CONTINUE
 4562 CONTINUE
 4561 CONTINUE
      NZUM=NZUM+1
      DO 4564 ILL=1,3
      PATPK(NOPTPK+NZUM,ILL)=DIFPK(JZ,ILL)
 4564 CONTINUE
      FREPTP(NZUM+NOPTPK)=1
 1108 CONTINUE
      IF(AMOD(JZ,NSYM).EQ.0) NUMSPK((JZ+NSYM-1)/NSYM,NJ)=NUM
  108 CONTINUE
  106 CONTINUE
      IF(MAPS.EQ.0) GO TO 39000
      DO 50001 KMA=1,AMULT(3)
      WRITE(6,50000) KMA
50000 FORMAT(1X,'SECTION NUMBER',I3)
      DO 50002 JMAA=1,50
      WRITE(6,60000)(MAP(IMA,JMAA,KMA),IMA=1,50)
60000 FORMAT(1X,50I1)
50002 CONTINUE
50001 CONTINUE
39000 CONTINUE
C
C***** WRITES OUT PATTERSIN PEAKS AND FREQUENCY OF ENCOUNTER.
C
      WRITE(6,205)
      DO 201 JB=1,NOPTPK+NZUM
       WRITE(6,200) (PATPK(JB,JBB),JBB=1,3),FREPTP(JB)
  201 CONTINUE
      IF(KNPKXN.EQ.1) GO TO 4002
C
C***** WRITES OUT PEAK AND NUMBER OF TIMES IT IS PRESENT.
C
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```
      WRITE(6,206)
      WRITE(6,1000)
      WRITE(6,7882)NKNAT+2,(SYM(10),J=1,NKNAT+2)
7882  FORMAT(1X,*A1)
      DO 202 JC=1,NOPK
      WRITE(6,203)(PEAK(JC,JCC),JCC=1,3),NUMPK(JC),NKNAT+2,SYM(10),
     *(SYM(NUMSPK(JC,NS)+1),NS=1,NKNAT),SYM(10)
      IF (SOLVE.EQ.0) GO TO 4999
      A=NUMSPK(JC,AMOD(JP,3)+1)
      B=NUMSPK(JC,AMOD(JP+1,3)+1)
      C=A+B
      IF(A.GT.1.AND.B.GT.1.AND.C.GT.NSYM/2) CHECK1(JC)=C
      IF(A.GE.NSYM/2+1.OR.B.GT.NSYM/2+1) CHECK2(JC)=C
      IF(CHECK2(JC).EQ.CHECK1(JC))CHECK2(JC)=0
4999  CONTINUE
 202  CONTINUE
      WRITE(6,7882)NKNAT+2,(SYM(10),J=1,NKNAT+2)
4002  CONTINUE
      IF(SOLVE.EQ.1) GO TO 8000
      IF (PID.EQ.1) GO TO 8000
      IF(SOLVE.NE.1) GO TO 5065
5604  CONTINUE
5065  CONTINUE
      IF(PID.EQ.1) GO TO 10000
      PSYMR=1
      PID=1
      IF(SOLVE.EQ.2) GO TO 6000
      IF(KNPKXN.EQ.0) GO TO 10000
      NO=0
      M=0
      GO TO 605
 804  CONTINUE
      NO=NO+1
      IF(NO.EQ.NKNAT) GO TO 807
 605  CONTINUE
      WRITE(6,803)
      N=0
      DO 606 JW=1,(NUMNO2-NUMNO1)*NSYM
      IF(NUMPK(JW).NE.NKNAT-NO) GO TO 606
      N=N+1
      WRITE(6,801) (PEAK(JW,IB),IB=1,3),JW,NKNAT,NKNAT-NO
      DO 607 IA=1,3
      KNATOM(N+NUMNO2,IA) =PEAK(JW,IA)
 607  CONTINUE
 606  CONTINUE
      NNKNAT=NNKNAT+N
      GO TO 804
 807  CONTINUE
 604  CONTINUE
      GO TO 8001
8000  CONTINUE
      DO 8009 JH=1,NOPTPK
      IF(CHECK2(JH).GT.NSYM/2.AND.CHECK3(JH).GE.NSYM/2-1) CHECK1(JH)=1+
     *CHECK3(JH)
8009  CONTINUE
      NUMA=0
      NUMACC=0
      WRITE(6,8008)
      DO 8002 JT=1,NOPTPK
      IF(CHECK1(JT).EQ.0) CHECK1(JT)=CHECK2(JT)
      IF(CHECK1(JT).EQ.0.AND.CHECK2(JT).EQ.0) GO TO 8002
      DO 8005 JE=1,NUMACC
      DO 8004 IS=1,NSYM
      NUMZ=0
      DO 8003 IM=1,3
      IF(AMOD(ABS(PEAK(JT,IM)-(APEAK(JE,IM)*SYMRL(IS,2*IM)+SYMRL(IS,2*IM
     *-1)))+TOLNC(IM),1).LT.2*TOLNC(IM)) NUMZ=NUMZ+1
      IF(NUMZ.EQ.3) GO TO 8002
```

```
 8003 CONTINUE
 8004 CONTINUE
 8005 CONTINUE
      NUMA= NUMA +1
      NUMACC=NUMA
      DO 8006 IZ=1,3
      APEAK(NUMA   ,IZ)=PEAK(JT,IZ)
 8006 CONTINUE
      RATING(NUMA  )=AMAX1(CHECK1(JT),RATING(JE))
      WRITE(6,8007)(APEAK(NUMA   ,IZ),IZ=1,3),RATING(NUMA  )
 8002 CONTINUE
      KOUNT=0
      DO 6502 JT=1,NUMACC
      DO 6505 JE=1,MKNAT
      DO 6504 IS=1,NSYM
      NUMZ=0
      DO 6503 IM=1,3
      IF(AMOD(ABS(KNATOM(JE,IM)-(APEAK(JT,IM)*SYMRL(IS,2*IM)+SYMRL(IS,
     *2*IM-1)))+TOLNC(IM),1).LT.2*TOLNC(IM))NUMZ=NUMZ+1
      IF(NUMZ.EQ.3) GO TO 6502
 6503 CONTINUE
 6504 CONTINUE
 6505 CONTINUE
      KOUNT=KOUNT+1
      DO 6506 IZ=1,3
      KNATOM(MKNAT+KOUNT,IZ)=APEAK(JT,IZ)
 6506 CONTINUE
 6502 CONTINUE
      MKNAT=MKNAT+KOUNT
      WRITE(6,6510)
 6510 FORMAT(1X,'LIST OF KNOWN ATOM POSITIONS AT THIS POINT')
      DO 6511 JT=1,MKNAT
      WRITE(6,6512)(KNATOM(JT,IM),IM=1,3)
 6512 FORMAT(10X,3F10.6)
 6511 CONTINUE
      NKNAT=MKNAT
      IF(MKNAT.GT.NPNAT)NPNAT=NPNAT+1
 8001 CONTINUE
      GO TO 5604
10000 CONTINUE
      STOP
      END
```

```
C      PROGRAM ARTSTC
C      **************
C
C
C           PROGRAM TO PRODUCE A SHADED ELECTRON DENSITY MAP FROM DATA
C           PRODUCED IN A FOURIER PROGRAM.  ANY NUMBER OF COPIES OF
C           SECTIONS MAY BE PRODUCED. A GRID FOR DETERMINATION OF
C           COORDINATES IS ALSO PRODUCED.
C           MARK 2 VERSION SEPTEMBER 1975
C           WRITTEN BY D.L.EVANS UNIVERSITY OF CANTERBURY MARCH 1974
C           REVISED SEPTEMBER 1975 COPYRIGHT HELD BY THE AUTHOR.
C
C      FEATURES
C      ********
C      1. DENSITY PROFILE - PRINTED FOR EACH SECTION
C      2. INTERPOLATION - (1) FOR INCREASED SMOOTHING AND (2) TO MINIMISE
C         TOPOLOGICAL DISTORTION DUE TO FIXED PRINT POSITION,CHARACTER
C         WIDTH, HEIGHT, AND LINE SPACING CHARACTERISTICS.
C      3. ON REQUEST PRINTS A GRID USEFUL AS AN AID TO READING
C         COORDINATES.
C      4. PRINTS ADDITIONAL COPIES ON REQUEST (AND ALSO SUPPLIES A GRID).
C      5. PRINTS CELL DIMENSIONS AND CM. TO ANG. CONVERSION FACTORS,
C      6. FRACTIONAL COORDINATES ARE LISTED FOR THE CALCULATED POINTS.
C      7. REPRODUCES CELL ANGLES IN THE RANGE 45DEG. TO 135DEG. TO WITHIN
C      0.1DEGREE.
C      8. CAN PRINT MAPS OF ANY LENGTH,WIDTH LIMITED BY PAPER WIDTH.
C      9. CONTOURS CAN BE MADE BY TRACING AROUND REGIONS
C         CONTAINING THE SAME SHADING CHARACTER.
C      10. MAXIMUM AND MINIMUM DENSITY LEVELS CAN BE VARIED FOR SPECIFIC
C         PURPOSES,WHICH VARIES THE NUMBER OF SHADES SPREAD ACROSS
C         REGIONS OF THE MAP.
C      11. THE DARKEST SHADE IN EACH COLUMN OF CALCULATED VALUES IS
C         PRINTED OUT AT THE BOTTOM OF EACH MAP AS AN AID TO LOCATION OF
C         POINTS OF HIGH DENSITY.
C      12. THE COMPLETE LIST OF SHADES IS GIVEN IN THE HEADING OF EACH
C         MAP.
C
C      PROGRAM CONTROL.          VALUES OF CONTROL INTEGERS
C      ****************
C      USER OPTIONS            BY DEFAULT          USER
C      RANGE OF DENSITY        0 TO 1000    -1000<RHOMIN<RHOMAX<1000
C      NUMBER OF COPIES            1                1 - 8
C      GRID                      0,2 TO 8           9
C          ** NOTE THAT THE NUMBER OF COPIES AND THE GRID ARE SPECIFIED
C           USING THE SAME CONTROL INTEGER
C
C      INPUT                                          FORMAT 3I5
C      *****                                          **********
C      NUMPIC(NO. OF COPIES (OR 9 FOR A GRID WITH ONE COPY))
C      RHOMAX
C      RHOMIN
C
C
C      DETAILS OF THE FILE STRUCTURE
C      *****************************
C
C      THE FIRST RECORD CONTAINS INFORMATION ON LIMITS, INCREMENTS AND
C      ORIENTATION AS DETAILED BELOW.
C       NX    THE NUMBER OF POINTS ACROSS A LINE OF A SECTION.
C       NY THE NUMBER OF ROWS/SECTION.
C       NZ    THE NUMBER OF SECTIONS.
C
C      NORIEN   100 SECTION COMPUTED ALONG THE X AXIS
C                10 SECTION COMPUTED ALONG THE Y AXIS
C                 1 SECTION COMPUTED ALONG THE Z AXIS.
C      ADDITIONAL NOTE CONCERNING NORIEN
C
C      NORIEN        FASTEST        LINE        SECTION
```

```
C                    VARYING          INDEX          INDEX
C                  (ACROSS PAGE)   (DOWN PAGE)
CCC      100             Z              Y              X
CCC       10             X              Z              Y
CCC        1             Y              X              Z
CCCC
```

```
      DIMENSION TITLE(124,6)
      DIMENSION INDX(3)
      DIMENSION INDIC(3)
      DIMENSION PRNTAA(126,205)
      DIMENSION ANGLE(10,135)
      DIMENSION NOVER(1103)
      DIMENSION DJ(150),G(38)
      DIMENSION D(21),ARTSTC(8,38),MTONEF(1103),VAL(3,125)
      DIMENSION ALPHAR(10),BETAR(10),CINTER(4,3,130),RINTER(5,3,125)
      DIMENSION TINTER(4,5,125)
      DATA NPNP2/1,2,2,3,4/
      DATA G/1,1,1,1,2,2,2,2,2,2,2,2,3,4,5,5,6,6,7,8,1,1,1,1,1,1,1,1,
     *1,1,1,1,1,1,1,1,1/
      DATA INDIC/'Y','X','Z'/
      DATA D/0,50,100,150,200,250,300,350,400,450,500,550,600,650,700,75
     *0,800,850,900,950,1000/
      DATA ARTSTC/' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     1' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     1'_',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     1'+',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     1')',' ','(',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     1'1',' ','_',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     1'M',' ','-',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     1'Z',' ','-',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     1'O',' ','-',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     1'O',' ','+',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     1'A',' ','-',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     1'X',' ','-',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     1'O',' ','=',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     1'O',' ','+',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     1'O',' ','+',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     1'O',' ','+',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     1'O',' ','X',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     1'O',' ','X',' ',' ',' ','H',' ','C',' ',' ',' ',' ',' ',' ',' ',
     1'O',' ','X',' ',' ',' ','H',' ','B',' ',' ',' ',' ',' ',' ',' ',
     1'O',' ','X',' ',' ',' ','H',' ','B',' ','V',' ',' ',' ',' ',' ',
     1'O',' ','X',' ',' ',' ','H',' ','B',' ','V',' ','A',' ',' ',' ',
     *'0',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     *'1',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     *'2',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     *'3',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     *'4',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     *'5',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     *'6',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     *'7',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     *'8',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     *'9',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     *'Y',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     *'X',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     *'Z',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     *' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     *'.',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     *'_',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',
     *'+',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' ',' '/
C
C
      NUMPIC=ISST(4)
C     INITIALISES PROGRAM PARAMETERS
C
      IF(NUMPIC .GE. 2)  GRIDNM = 1
      IF (NUMPIC .EQ.9) NUMPIC = 1
      B = 1
      C = 2
C
C     ASSIGNS 20 SHADESTO RANGES OF VALUES 0-1000 AND ASSESSES NUMBER OF
C     OVERPRINTINGS FOR EACH SHADE
C
      DO 100 NVALUE = 1,1000
```

```
      DO 200 SIZE = 1,20
      IF (NVALUE .GT. D(SIZE) .AND. NVALUE .LE. D(SIZE+1)) GO TO 298
  299 GO TO 297
  298 CONTINUE
      MTONEF(NVALUE) = SIZE+1
      NOVER(NVALUE)= G(SIZE+1)
  297 CONTINUE
  200 CONTINUE
  100 CONTINUE
      DO 1700 NVALUE = 1087,1103
      SIZE = NVALUE-1066
      MTONEF(NVALUE) = SIZE+1
      NOVER(NVALUE) = G(SIZE+1)
 1700 CONTINUE
      IVXX = 1
C
C       READS FIRST RECORD OF FILE
C
      READ(IVXX,END=99) NX,NY,NZ,NORIEN,XMIN,XMAX,YMIN,YMAX,ZMIN,ZMAX
   99 CONTINUE
      NXX = NX
      NYY = NY
      YYMAX = YMAX
      YYMIN = YMIN
      XXMAX = XMAX
      XXMIN = XMIN
C
C       READS FILE TO END TO ENABLE THE READING OF THE LAST RECORD
C
      DO 2000 JKL = 1,NY*NZ
      READ(IVXX,END=1111) DUMMY
 1111 CONTINUE
 2000 CONTINUE
C
C      READS LAST RECORD
C
      READ(IVXX,END=1112) RMAX,(CELL(I),I=1,6)
 1112 CONTINUE
C
C      REWINDS FILE
C
      REWIND IVXX
C
C      READS FIRST RECORD TO BE READY FOR MAP RECORDS
C
      READ(IVXX,END=1113) DUMMY
 1113 CONTINUE
C
C      OBTAINS CELL ANGLES FROM THEIR COSINES
C
      DO 771 I = 4,6
      CELL(I) = ARCOS(CELL(I))*180.0/3.14159
  771 CONTINUE
C
C      INTERPRETS NORIEN
C
      DO 456 NNM = 1,3
      DIV = NORIEN/(10**(NNM-1))
      IF (DIV .EQ. 1.0) NNMM = NNM
  456 CONTINUE
      DO 457 JKL = NNMM,NNMM+2
      NA = JKL-NNMM+1
      INDX(NA) = INDIC(MOD(JKL,3)+1)
      INDXA(NA) = MOD(JKL,3) + 1
  457 CONTINUE
      NOPOIN = NX
C
C      OBTAINS ANGLE FOR THE SECTIONS TO BE PRINTED
```

```
C
      ANGIN = CELL(7-NNMM)
      DIFANG = 50.0
C
CC    SETS PROGRAM PARAMETERS ACCORDING TO WHETHER ANGLE IS OBTUSE OR
CCC   ACUTE
C
      ACTANG = ANGIN-90.0
      J1 = 0
      J2 = 1
      IF (ACTANG .LT. 0) GO TO 1802
      GO TO 1801
 1802 CONTINUE
      J1 = 1
      J2 = -1
 1801 CONTINUE
      ACTANG = ABS(ACTANG)
C
CC    OBTAINS TANGENT OF ANGLE AS A RATIONAL FRACTION
C
      DO 301 N = 1,10
      DO 302 M=1,135
      ANGLE(N,M) = 180.0*(ATAN(1.25*FLOAT(N)/M))/3.14159
      IF (ABS(ANGLE(N,M)-ACTANG) .LT. DIFANG) GO TO 303
      GO TO 306
  303 CONTINUE
      WTDANG = ANGLE(N,M)
      NANG = N
      MANG = M
      DIFANG = ABS(ANGLE(N,M) -ACTANG      )
  306 CONTINUE
  302 CONTINUE
  301 CONTINUE
C
CCC   DETERMINES SCALING FACTORS
CCCC
CCCC  MAKES DECISIONS AS HOW BEST TO EXPAND THE MAP,BY WHAT AMOUNT AND
CC    WHICH WAY TO ORIENT IT
C
      SCALE1= 999.0/RMAX
      SCALE2 = 999.0/(RHOMAX-RHOMIN)
C
CC    READS IN A SECTION OF THE MAP FROM THE FILE
C
      IF(NEND.EQ.0) GO TO 11003
      DO 11000  K=1,NEND
      DO 11001 J=1,NY
      READ(IVXX,END=11002) DUMMY
11002 CONTINUE
11001 CONTINUE
11000 CONTINUE
11003 CONTINUE
      IF(NOSECT.EQ.0) NOSECT=NZ
      DO 97 JSECT=NEND+1,NOSECT
      ROWN = 0
      DO 827 JP = 1,5
      JPJ = 6-JP
      JDIVX = 125/NXX
      JDIVY = 125/NYY
      IF (JDIVX .GE. JPJ) GO TO 829
      IF (JDIVY .GE. JPJ) GO TO 898
  827 CONTINUE
      GO TO 849
  898 CONTINUE
      DO 227 KK = 1,NYY
      READ(IVXX,END=119)(SECT(K,KK),K=1,NXX)
  119 CONTINUE
```

```
  227 CONTINUE
      NX = NYY
      NY = NXX
      NOPOIN = NX
      JSCACR = 1
      JSCDOW = 3
      YMAX = XXMAX
      XMAX = YYMAX
      YMIN = XXMIN
      XMIN = YYMIN
      LENDOW = CELL(MOD(5-NNMM,3)+1)
      LENACR = CELL(MOD(4-NNMM,3)+1)
C
CCC   NP IS THE EXPANSION FACTOR ACROSS THE PAGE
CCC   NP2 IS THE EXPANSION FACTOR DOWN THE PAGE
C
      NP = 5
      IF (JDIVY .LT. 5) NP=JDIVY
      NP2 = NPNP2(NP)
      DIV1 = FLOAT(NP)/NP2
      ANG = 1.25*COS((3.14159*ACTANG)/180.0)
      IF(ABS(DIV1-ANG)/DIV1 .GT.ABS(1.0-ANG))NP2=NP
      GO  TO 839
  829 CONTINUE
      JSCDOW = 1
      JSCACR = 3
C
CCCC  OBTAINS CELL LENGTHS DOWN AND ACROSS THE PAGE
C
      LENACR = CELL(MOD(5-NNMM,3)+1)
      LENDOW = CELL(MOD(4-NNMM,3)+1)
      DO 116 KK = 1,NY
      READ(IVXX,END=115)(SECT(KK,K),K=1,NX)
  115 CONTINUE
  116 CONTINUE
      NP = 5
      IF(JDIVX .LT.5) NP = JDIVX
      NP2 = NPNP2(NP)
      DIV1 = FLOAT(NP)/NP2
      ANG = 1.25*COS((3.14159*ACTANG)/180.0)
      IF(ABS(DIV1-ANG)/DIV1 .GT.ABS(1.0-ANG))NP2=NP
  849 CONTINUE
  839 CONTINUE
C
CCC   CALCULATES THE NUMBER OF 'ROWS' TO MOVE EACH 'COLUMN' OF AN ARRAY
CCC   'UPWARDS' TO OBTAIN THE ANGLE IN THE MAP
C
      DO 1777 NPLACE = 1,(NX-1)*NP+1
      NM = FLOAT(MANG)/NANG + 0.5
      IF(NANG .GE. 0.5*FLOAT(MANG)) GO TO 311
      GO TO 312
  311 CONTINUE
      NOOF2S = MANG-NANG
      NOOF1S = NANG-NOOF2S
      NL = FLOAT(MANG)/NOOF2S+0.5
      DO 313 AL = 1,NL*NOOF2S,NL
      IF(MOD(NPLACE,MANG) .EQ. AL-1) GO TO 416
  313 CONTINUE
      NUP = NUP+1
  416 CONTINUE
      GO TO 402
  312 CONTINUE
      DO 400 MM = 1,NM*NANG,NM
      IF (MOD(NPLACE,MANG) .EQ. MM-1) NUP = NUP+1
  400 CONTINUE
  402 CONTINUE
      MPLACE = J1*((NX-1)*NP+2)+J2*(NPLACE)
```

```
      NNUP(MPLACE) = NUP
 1777 CONTINUE
      SCALEY = (XMAX-XMIN)*10.0*LENACR/(2.54*((NX-1)*NP+1))
      SCALEZ = (YMAX-YMIN)*8.0*LENDOW/(2.54*((NY-1)*NP2+1))
C
CC    OBTAINS CM/ANG. CONVERSION SCALES
C
      CHARCY = (YMAX-YMIN)*LENDOW/((NY-1)*NP2)
      CHARCZ = (XMAX-XMIN)*LENACR/((NX-1)*NP )
      UPNUM = NX*NP*FLOAT(NANG)/MANG + 15
      IF (NUMPIC .LT. 2) NUMPIC = 1
C
CC    BEGINNING OF SECTION TO MAKE NUMPIC COPIES OF EXPANDED MAPS
C
      DO 773 JJM = 1,NUMPIC
C
CC    WRITES OUT HEADER INFORMATION FOR EACH SECTION INCLUDING CELL
CCC   CONSTANTS,RMAX AND A LEGEND FOR THE SHADING
C
      START1 = 56
      START2 = START1
      WRITE(6,1833)
 1833 FORMAT(1H1,' ')
      WRITE(6,601)
  601 FORMAT(1X,' ')
      WRITE(6,502)(START1,(ARTSTC(JJ,       KKK ),KKK=2,21),JJ=1,8)
  502 FORMAT((1H+,*X,20A1))
      IF (NZ .LT. 2) GO TO 832
      SECTIN = (ZMAX-ZMIN)*(JSECT-1)/(NZ-1) + ZMIN
      GO TO 833
  832 CONTINUE
      SECTIN = ZMIN
  833 CONTINUE
      IF (GRID .EQ. 1) WRITE(6,1503)
 1503 FORMAT(1X,41X,'THIS IS AN OVERLAY GRID FOR DETERMINATION OF COORDI
     *NATES')
      IF (GRID .NE. 1) WRITE(6,503) SCALE1,INDX(2),SECTIN,RMAX
  503 FORMAT(1X,'C = ',E10.3,42X' *     'A1,' = 'F5.2,'     * ',35X,'RMAX
     *='E15.3)
      WRITE(6,600)
  600 FORMAT(1X,' ')
      WRITE(6,504)(START1,(ARTSTC(JJ,       KKK ),KKK=2,21),JJ=1,8)
  504 FORMAT((1H+,*X,20A1))
      WRITE(6,599)
  599 FORMAT(/,1X,' ')
      WRITE(6,772) (CELL(I),I=1,6)
  772 FORMAT(1H,'CELL PARAMETERS   A = 'F5.2,'  B = 'F5.2,'  C = 'F5.2,'
     *  ALPHA = 'F6.2,'    BETA = 'F6.2,'    GAMMA = 'F6.2)
      IF(ANGIN .LT. 89.0 .AND. JSECT .EQ. 1 .AND. (NUMPIC .EQ. 9 .OR.
     *NUMPIC .EQ.1)) WTDANG = -WTDANG
      IF (ABS(ANGIN-90.0) .LT. 1.0) WTDANG = 0.0
      WRITE(6,775) SCALEZ,SCALEY,WTDANG+90.0,JJM
  775 FORMAT(/,1X,'PLOT PARAMETERS   COLUMN SCALE = ',F4.2,' ANGSTROMS/C
     *M   HORIZ. ROW SCALE = ',F4.2,' ANGSTROMS/CM   SECTION ANGLE = 'F5
     *.1,'   COPY NUMBER',I3)
      WRITE(6,3776)
 3776 FORMAT(1X,39X,'.',32X,'.')
      WRITE(6,3777) CHARCY,CHARCZ
 3777 FORMAT(1X,34X,1F5.3,'A/CHARACTER',17X,1F5.3,'A/CHARACTER')
C
CC     PLACES THE ACROSS THE PAGE SCALE IN AN ARRAY TO ENABLE IT TO BE
CC    WRITTEN OUT 'VERTICALLY'
C
      DO 700 PLACE = 1,NOPOIN
      ACROSS(PLACE) = (PLACE-1)*(XMAX-XMIN)/(NX-1) + XMIN
      IF(ACROSS(PLACE) .GE. 0) GO TO 157
      PLM(PLACE) = 1102
      GO TO 159
```

```
  157 CONTINUE
      PLM(PLACE) = 1103
  159 CONTINUE
      BB(PLACE) = ABS(ACROSS(PLACE))*1000
      AA(PLACE) = MOD(BB(PLACE),10)+0.5
      CC(PLACE) = (BB(PLACE)-AA(PLACE))/10
      DD(PLACE) = MOD(CC(PLACE),10)
      EE(PLACE) = (CC(PLACE) - DD(PLACE))/10
  700 CONTINUE
      DO 4477 JKLM = 1,150
      DJ(JKLM)=1
 4477 CONTINUE
  962 CONTINUE
C
CC    SETS PRINTOUT ARRAY TO VALUE CORRESPONDING TO BLANK
C
      DO 561 JJJB=1,205
      DO 560 JJJA = 1,126
      PRNTAA(JJJA,JJJB) = 1100
  560 CONTINUE
  561 CONTINUE
      DO 563 JACROS  = 1,NOPOIN
      TITLE(JACROS,1) = INDXA(JSCACR) + 1096
      TITLE(JACROS,2) =    PLM(JACROS)
      TITLE(JACROS,3) = 1101
      TITLE(JACROS,4) = EE(JACROS)   +1087
      TITLE(JACROS,5) = DD(JACROS) +1087
      TITLE(JACROS,6) = AA(JACROS)  +1087
C
CC    PLACES ACROSS THE PAGE SCALE IN PRINTOUT ARRAY ON THE SAME SLANT
CC    AS THE MAP TO FOLLOW
C
      DO 565 RROW = 1,6
      ROW = UPNUM+RROW-12
      NPLACE = (JACROS-1)*NP + 1
      ROWE = ROW-NNUP(NPLACE)
      PRNTAA(NPLACE,ROWE)=TITLE(JACROS,RROW)
      MEM2(ROWE)=1
  565 CONTINUE
  563 CONTINUE
C
CC    SETS PROGRAM PARAMETERS TO ENABLE THE EXPANDED MAP TO BE
CC    CREATED IN SUCCESSIVE SECTIONS
C
      OOTROW=0
       ROW = UPNUM + 1
      NUMN = (200.0-UPNUM)/NP2
      NUM1 = 1
      NUM2=NUMN+1
      IF (GRID .EQ. 1) NUM2 = NUMN
      BOTNUM = 200-MOD(200-UPNUM,NP2)
      NOROW=UPNUM+(NY-1)*NP2+1
      IF(NY+1 .LT. NUM2) NUM2 = NY+1
      GO TO 90
   91 CONTINUE
      ROW =UPNUM-14
      NOROW = ROW+NOROW-BOTNUM
      BOTNUM=(200.0/NP2)*NP2
      NUMN=200.0/NP2
      NUM1 = 1+NUM2
      NUM2 = NUM1 + NUMN
      IF (NY+1 .LT. NUM2) NUM2 = NY+1
   90 CONTINUE
C
CC    BEGINNING OF INTERPOLATION PROCEDURE
C
      DO 98 KK = NUM1,NUM2
C
```

```
C       MANIPULATES INFORMATION RETAINED FROM THE PREVIOUS ROW DEALT WITH
C
      IF (GRID .EQ. 1) GO TO 958
      DO 4999 M=1,KFLAG1
      IF(M.EQ.0) GO TO 4998
      A1(M,B)=0.0
      A2(M,B)=0.0
 4999 CONTINUE
 4998 CONTINUE
      DO 5100 M=1,KFLAG2
      IF (M.EQ.0) GO TO 5101
      A1(M,B)=A1(M,C)
      A2(M,B)=A2(M,C)
      A1(M,C)=0.0
      A2(M,C)=0.0
 5100 CONTINUE
 5101 CONTINUE
      KFLAG1=KFLAG2
      JMM=0
 5008 JMM=JMM+1
      DO 110 K=A1(JMM,1),A2(JMM,1)
      IF(K.EQ.0) GO TO 110
      PLACE = K
      DO 125 PTNO = 1,NP-1
      RINTER(PTNO,B,K) = RINTER(PTNO,C,K)
      RINTER(PTNO,2,K)=1
      NPLACE = (PLACE-1)*NP + 1 + PTNO
      ROWE=ROW-NNUP(NPLACE)
      PRNTAA(NPLACE,ROWE             )=RINTER(PTNO,1,PLACE)
      MEM2(ROWE)=1
  125 CONTINUE
      NPLACE = (PLACE-1)*NP+1
      VAL(B,K) = VAL(C,K)
      VAL(2,K)=1
      ROWE=ROW-NNUP(NPLACE)
      PRNTAA(NPLACE,ROWE             )=VAL(1,K)
      MEM2(ROWE)=1
      IF(JMM.EQ.KFLAG1) GO TO 110
      IF(K.EQ.A2(JMM,1)) GO TO 5008
  110 CONTINUE
  112 CONTINUE
      IF(KK.EQ.NY+1) GO TO 98
C
CC    SCALES INPUT VALUES
C
      DO 124 K = 1,NX
      VAL(C,K) = (SECT(KK,K)*SCALE1-RHOMIN)*SCALE2
  124 CONTINUE
C
CC    ASSESSES ROW FOR REGIONS WHICH ARE TO BE INTERPOLATED
C
      K=0
      FLAG=0
      DO 122 PLACE = 1,NX
      JLN=PLACE
      IF (VAL(C,PLACE) .GT. 1000) VAL(C,PLACE) = 999
      IF (VAL(C,PLACE) .LT. 1) VAL(C,PLACE) = 1
      IF (VAL(C,PLACE).GT.1) GO TO 5000
      FLAG=0
      GO TO 122
 5000 CONTINUE
      IF(FLAG.EQ.0) K=K+1
      A1(K,C)=(JLN-1)*(1-FLAG)+A1(K,C)
      IF(JLN.EQ.1) A1(K,C)=1
      A2(K,C)=(A1(K,C)  )*(1-FLAG)+A2(K,C)+1*FLAG
      IF(JLN.EQ.NOPOIN) A2(K,C)=NOPOIN
      FLAG=1
  122 CONTINUE
```

```
      KFLAG2=K
      JMM=0
 5002 JMM=JMM+1
C
C     INTERPOLATES ACROSS A ROW OF GRIDPOINTS
C
      DO 102 PLACE=A1(JMM,C),A2(JMM,C)
      IF (PLACE.EQ.0) GO TO 102
      IF(                          VAL(C,PLACE).GT.DJ(PLACE))DJ(PLACE)=VAL(
     *C,PLACE)
      DO 103 PTNO = 1,NP-1
      RINTER(PTNO,C,PLACE) =((NP-PTNO)*VAL(C,PLACE) + PTNO*VAL(C,PLACE+1
     *))/NP
      IF (RINTER(PTNO,C,PLACE) .LT. 1.0) RINTER(PTNO,C,PLACE) = 1
      IF (RINTER(PTNO,C,PLACE) .GT. 1000) RINTER(PTNO,C,PLACE) = 999
  103 CONTINUE
      IF(JMM.EQ.KFLAG2) GO TO 102
      IF(PLACE.EQ.A2(JMM,C)) GO TO 5002
  102 CONTINUE
      DO 5004 JKL=1,NOPOIN
      MEM(JKL)=0
 5004 CONTINUE
 4020 IF(KK .LT. 2 ) GO TO 98
 4021 CONTINUE
C
C     REMEMBERS AREAS BETWEEN ROWS FOR WHICH VALUES ARE TO BE CALCULATED
C     BY A LINEAR INTERPOLATION
C
      IF(KFLAG1.EQ.0) GO TO 5900
      DO 5005 N=1,KFLAG1
      DO 5006 LN=A1(N,B),A2(N,B)
      MEM(LN)=1
 5006 CONTINUE
 5005 CONTINUE
 5900 CONTINUE
      IF(KFLAG2.EQ.0) GO TO 5901
      DO 5007 N=1,KFLAG2
      DO 5009 LL=A1(N,C),A2(N,C)
      MEM(LL)=1
 5009 CONTINUE
 5007 CONTINUE
 5901 CONTINUE
C
C     CARRIES OUT THE INTERPOLATION CALCULATIONS FOR THE IN-BETWEEN ROWS
C     AND PLACES THE RESULTS IN THE PRINTOUT ARRAY
C
      CJ = 1
      MPLACE = 1
      IF(KFLAG1.EQ.0.AND.KFLAG2.EQ.0) GO TO 998
      DO 104 PLACE = 1,NOPOIN
      IF(MEM(PLACE).EQ.0) GO TO 6104
      DO 106 DPTNO = 1,NP2 -1
      CINTER(DPTNO,B,PLACE) =((NP2-DPTNO)*VAL(B,PLACE)+DPTNO*VAL(C,PLACE
     *))/NP2
      IF(CINTER(DPTNO,1,PLACE) .LT.1.0) CINTER(DPTNO,1,PLACE) = 1
      IF(CINTER(DPTNO,1,PLACE)  .GT.1000) CINTER(DPTNO,1,PLACE)= 999
      ROWA=ROW+DPTNO-NNUP(MPLACE)
      PRNTAA(MPLACE,ROWA              )=CINTER(DPTNO,1,PLACE)
      CINTER(DPTNO,1,PLACE)=0
      MEM2(ROWA)=1
      DO 117 PTNO = 1,NP-1
      TINTER(DPTNO,PTNO,PLACE)=((NP2-DPTNO)*RINTER(PTNO,B,PLACE)+DPTNO*R
     *INTER(PTNO,C,PLACE))/NP2
      IF (TINTER(DPTNO,PTNO,PLACE).LT. 1.0)TINTER(DPTNO,PTNO,PLACE)=1
      IF(TINTER(DPTNO,PTNO ,PLACE)  .GT.1000) TINTER(DPTNO,PTNO,PLACE)=
     * 999
      NPLACE = (PLACE-1)*NP + 1 + PTNO
      ROWA = ROW+DPTNO-NNUP(NPLACE)
```

```
      PRNTAA(NPLACE,ROWA              )=TINTER(DPTNO,PTNO,PLACE)
  117 CONTINUE
  106 CONTINUE
      DO 1117 PTNO=1,NP-1
      RINTER(PTNO,B,PLACE)=1.0
 1117 CONTINUE
 6104 CONTINUE
      MPLACE = MPLACE+NP
      VAL(1,PLACE)=1
  104 CONTINUE
      GO TO 998
  958 CONTINUE
C
CC    TO PRODUCE A GRID FOR LOCATING PEAKS EASILY
C
      DO 961 JJJAA = 1,(NX-1)*NP+1,NP
      ROWE= ROW-NNUP(JJJAA)
      PRNTAA(JJJAA,ROWE)=1101
      MEM2(ROWE)=1
  961 CONTINUE
  998 CONTINUE
      ROW = ROW+NP2
   98 CONTINUE
      IF(NOROW.LE.200)IEND=NOROW+4
      IF(NOROW.LE.200)SHADER=IEND
      IF(NOROW.GT.200)IEND=BOTNUM
      IF(NOROW.GT.200)SHADER=205
      IF(NOROW.GT.200)  GO TO 778
      NK=0
      DO 777 NPLACE =1,NOPOIN*NP,NP
      NK=NK+1
      ROWE = SHADER-NNUP(NPLACE)
      PRNTAA(NPLACE,ROWE)=DJ(NK)
      MEM2(ROWE)=1
  777 CONTINUE
  778 CONTINUE
      IF(NOROW.LE.200)ENDNUM=SHADER
      IF(NOROW.GT.200)ENDNUM=BOTNUM-(UPNUM-15)
      CUPNUM = UPNUM
      DO 197 ROW = 1,ENDNUM
      OUTROW = ROW+ OOTROW
  192 CONTINUE
      CJ=1
C
CC    DETERMINING MAXIMUM DENSITY WITHIN 'ORIGINAL' COLUMNS
C
      IF(MEM2(ROW).EQ.0) GO TO 5780
      DO 780 NPLACE=1,(NOPOIN-1)*NP+1
      IF(PRNTAA(NPLACE,   ROW).GT.CJ.AND.PRNTAA(NPLACE,   ROW).LT.1050)
     *CJ=PRNTAA(NPLACE,   ROW)
  780 CONTINUE
 5780 CONTINUE
      IF (ANGIN .LT. 90.0) UPNUM = 15
      IF(NP2.EQ.1.AND.OUTROW.GE.UPNUM+1)GO TO 47
      IF (MOD(OUTROW-UPNUM,NP2) .EQ. 1 .AND. OUTROW.GE.UPNUM+1) GO TO 47
      GO TO 48
   47 CONTINUE
      S1 = 120-((NX-1)*NP+1)
      INDEX = ((OUTROW-UPNUM)/NP2)*(YMAX-YMIN)/(NY-1)+YMIN
      IF (OUTROW .GE. NY*NP2+UPNUM) GO TO 1800
      WRITE(6,43) S1,INDX(JSCDOW),INDEX
   43 FORMAT(1X,*X,A1,' = ',F6.3 )
      GO TO 1799
 1800 WRITE(6,42)
 1799 CONTINUE
   48 CONTINUE
      IF (MOD(OUTROW-UPNUM,NP2) .NE. 1 .AND. OUTROW.GE.UPNUM+1) WRITE(6,
     *42)
```

```
 42 FORMAT(1X,'         ')
    IF(OUTROW.LE.UPNUM)WRITE(6,776)
776 FORMAT(1X,' ')
    S  = 132-((NX-1)*NP+1)
    IF (MEM2(ROW).EQ.0) GO TO 779
    WRITE(6,107)
   *(S,(NX-1)*NP+1,((ARTSTC(JJJ,MTONEF(PRNTAA(PLACE,   ROW))),PLACE=1,
   *(NOPOIN-1)*NP+1)),JJJ=1,NOVER(CJ))
107 FORMAT((1H+, *X,*A1))
779 CONTINUE
    DO 1979 NPLACE = 1,(NX-1)*NP+1
    PRNTAA(NPLACE,ROW) = 1100
1979 CONTINUE
197 CONTINUE
    OOTROW=OUTROW
    UPNUM = CUPNUM
    IF (UPNUM .EQ. 15) GO  TO 196
    DO 198 ROW = BOTNUM+16-UPNUM,BOTNUM
    NROW = ROW- (BOTNUM+15-UPNUM)
    DO 195 NPLACE = 1,(NX-1)*NP+1
    PRNTAA(NPLACE,NROW) = PRNTAA(NPLACE,ROW)
195 CONTINUE
    MEM2(NROW)=MEM2(ROW)
198 CONTINUE
196 CONTINUE
    IF (NUM2 .LT.  NY+1) GO TO 91
    NUP = 0
    IF (ABS(ANGIN-90.0) .LT. 1.0) GO TO 769
769 CONTINUE
    IF (GRID .EQ. 1) GO TO 96
773 CONTINUE
 97 CONTINUE
    IF (GRIDNM .EQ. 1) GRID = 1
    IF (GRIDNM .NE. 1) GO TO 96
    WRITE(6,859)
859 FORMAT(1H1,' ')
    GO TO 962
 96 CONTINUE
    RETURN
    END
```

```
PROGRAM SORTLIST

ALGOL SUBROUTINE
$ SET LIBRARY  $ LEVEL 3
   [FILE FILE2(KIND=DISK);
   FILE FILE6(KIND=PRINTER);
   REAL TEMP;
   ARRAY MLL[0:40,0:40];
 ]
REAL PROCEDURE LABELL(L,M,LL);VALUE L,M,LL;REAL L,M,LL;
BEGIN
DEFINE BASEF=[47:BLENGTH ] #,
       BLENGTH=12 #; %%%%%%%%% THIS  MUST  BE 47-MAX1  %%%%%%%
LABELL:=IF BOOLEAN((TEMP:=MLL[LL-1,M-1]).[L-1:1])THEN TEMP.BASEF+ONES
    (TEMP.[L-1:L]) ELSE 0;
END;
PROCEDURE SETUP(N,MIN,MAX,DATA,IHKL);REAL N;ARRAY MIN,MAX,DATA,IHKL[*];
BEGIN
ARRAY BUF[0:10];
DEFINE
BASEF=[47:47-MAX1] #,
FIRSTSORTED=FILE2 #,
INDEXF=[MAX1:MAX1+1] #,
MAX1=35 #,  %%%%%%% IF YOU CHANGE THIS ALSO CHANGE BLENGTH IN LABELL
MAX2=40 #,% IF YOU CHANGE THIS ALSO CHANGE  GLOBAL DIMENSIONS OF MLL
MAX3=40 #,% IF YOU CHANGE THIS ALSO CHANGE  GLOBAL DIMENSIONS OF MLL
ZEND=#;
INTEGER ARRAY DIF,BMIN,BMAX[0:2];
   REAL FIRST,SECOND,THIRD;
REAL INDX,INDEX2,NEWKEY,OLDKEY,COUNT;
BOOLEAN PROCEDURE SORTIN(RECD);ARRAY RECD[0];
  BEGIN
  IF READ(FIRSTSORTED,11,RECD)OR RECD[6] GEQ 99 THEN
    BEGIN
    SORTIN:=TRUE;
    END ELSE
    BEGIN
    RECD[FIRST]:=*+RECD[THIRD]*10000+RECD[SECOND]*100;
    END;
  END;
BOOLEAN PROCEDURE SORTCOMPARE(REC1,REC2);ARRAY REC1,REC2[0];
  SORTCOMPARE:= REC1[FIRST] LEQ REC2[FIRST];
PROCEDURE SORTOUT(BEOF,RECD);VALUE BEOF;
  BOOLEAN BEOF;ARRAY RECD[0];
  IF NOT BEOF THEN
    BEGIN
    RECD[FIRST]:=(NEWKEY:=RECD[FIRST])-RECD[SECOND]*100-RECD[THIRD]
        *10000;
    IF READLOCK(NEWKEY,OLDKEY)EQL NEWKEY THEN WRITE(FILE6,
      <"DUPLICATE RECORD FOR INDEXES ",3I5>,RECD[6],RECD[7],RECD[8])
    ELSE BEGIN
      REPLACE DATA[6*COUNT]BY POINTER(RECD[0]) FOR 6 WORDS;
      REPLACE IHKL[5*COUNT]BY POINTER(RECD[6]) FOR 5 WORDS;
      COUNT:=*+1;
    MLL[RECD[THIRD]-BMIN[THIRD-6],RECD[SECOND]-BMIN[SECOND-6]]:=*
      &1[RECD[FIRST]-BMIN[FIRST-6]:1];
      END;
    END ELSE
    BEGIN
    NEWKEY:=COUNT;
    REPLACE DATA[6*COUNT]BY POINTER(BUF[0]) FOR 6 WORDS;
    REPLACE IHKL[5*COUNT]BY POINTER(BUF[6]) FOR 5 WORDS;
    COUNT:=0;
    FOR INDX:=0 STEP 1 UNTIL BMAX[THIRD-6]-BMIN[THIRD-6]DO
    FOR INDEX2:=0 STEP 1 UNTIL BMAX[SECOND-6]-BMIN[SECOND-6]DO
      BEGIN
      MLL[INDX,INDEX2]:=*&COUNT BASEF;
      COUNT:=*+ONES(MLL[INDX,INDEX2].INDEXF);
```

```
      END;
    IF COUNT NEQ NEWKEY THEN WRITE(FILE6,<"MISSCOUNT IN SETUP",2I10>,
      COUNT,NEWKEY);
    END;
  IF NOT FIRSTSORTED.OPEN THEN FIRSTSORTED.FILETYPE:=7;
  READ(FIRSTSORTED,11,BUF);
  FOR INDX:=0,1,2 DO BMIN[INDX]:=BMAX[INDX]:=BUF[INDX+6];
  WHILE NOT READ(FIRSTSORTED,11,BUF)AND BUF[6]LSS 99 DO
    FOR INDX:=6,7,8 DO
      IF BMAX[INDX-6]LSS BUF[INDX]THEN BMAX[INDX-6]:=BUF[INDX]
      ELSE IF BMIN[INDX-6]GTR BUF[INDX]THEN BMIN[INDX-6]:=BUF[INDX];
    FIRST:=IF FIRST:=BMAX[0]-BMIN[0] LEQ SECOND:=
    BMAX[1]-BMIN[1]THEN IF FIRST LEQ BMAX[2]-BMIN[2]
    THEN 6 ELSE 8 ELSE IF SECOND LEQ BMAX[2]-BMIN[2]
    THEN 7 ELSE 8;
    SECOND:=CASE FIRST-6 OF (7,8,6);
    THIRD:=CASE FIRST-6 OF (8,6,7);
IF INDX:=FIRSTSORTED.RECORD GTR INDEX2:=REAL(NOT FALSE).BASEF THEN
       WRITE(FILE6,<I10," RECORDS READ BUT DIMENSIONED FOR ONLY",I10>
      ,INDX,INDEX2) ELSE
IF DIF[0]:=BMAX[FIRST-6]-BMIN[FIRST-6]GTR MAX1 OR
   DIF[1]:=BMAX[SECOND-6]-BMIN[SECOND-6] GTR MAX2 OR
   DIF[2]:=BMAX[THIRD-6]-BMIN[THIRD-6]GTR MAX3 THEN WRITE(FILE6,<"RANG)"
    ,3I5,"EXCEEDED ALLOWABLE DIMENSIONS",3I5>,DIF[0],DIF[1],DIF[2],
    MAX1,MAX2,MAX3)
ELSE BEGIN
  REWIND(FIRSTSORTED);
  OLDKEY:=0.5;
  SORT(SORTOUT,SORTIN,0,SORTCOMPARE,11,6000,100000);
  N:=COUNT;
  FOR INDX:=0,1,2 DO BEGIN MIN[INDX]:=BMIN[INDX];MAX[INDX]:=BMAX[INDX];
      END;
  END;
  END.
$SET SEPARATE AUTOBIND $
$ BIND = FROM SORTER
$USE LABEL FOR LABELL

FORTRAN MAINPROGRAM

FILE  2=XRC/IED,UNIT=DISK,BLOCKING=90,RECORD=11,AREA=900*5
C
C       UNIVERSITY OF CANTERBURY DEC. 1973.
C       WRITTEN BY D. L.EVANS.
C       FORTRAN PROGRAM WRITTEN FOR BURROUGHS B6700
C       PRODUCES STATISTICS BASED ON SINTHETA/LAMDA, FOBS,SIGMA,
C       MILLER INDICES AND PRINTS OUT A LISTING OF THE SORTED DATA
C
      REAL MTLDAT
      REAL MNFOBS
      REAL LAMDA
      REAL JSUM
      REAL LIMIT
      REAL OR,ORW, ORSUM1, ORSUM2,ORWSM1,ORWSM2
      INTEGER COUNT
      INTEGER VALM
      INTEGER Z, ZA, ZB, ZC
      INTEGER RAWDAT
      INTEGER VAL
      INTEGER OCC
      INTEGER SUMA, SUM
      INTEGER DATAA
      INTEGER C
      INTEGER DN, TOTNO, SNP, DNN, PNPP, B A, AJ,COLMAX
      INTEGER PARAM
      DIMENSION LIMIT(3,30)
      DIMENSION MMM(3)
      DIMENSION SCALE(6)
```

```
      DIMENSION TITLE(14)
      DIMENSION DIFF(3)
      DIMENSION SUM(30)
      DIMENSION LAMDA(3)
      DIMENSION JSUM(30)
      DIMENSION FSUM(30)
      DIMENSION FSQSUM(30)
      DIMENSION FCSQSM(30)
      DIMENSION NSUM(30)
      DIMENSION NUMPLN(3,30)
      DIMENSION CLSVAL(3,30)
      DIMENSION NONCLS(3,30)
      DIMENSION MIN(3), MAX(3)
      DIMENSION OCC(2000,3)
      DIMENSION DATA(6,4000),IHKL(5,4000),DATAA(4000)
      DIMENSION PUBDAT(4,12,1300)
      DIMENSION C1(3), C2(3), C3(3), C4(3), C5(3), C6(3)
      DIMENSION HKLSUM(45),HKFSUM(45),HKSQSM(45),HKQSUM(45),COUNT(45)
      DIMENSION ERROR(45)
      INDEX1 = 21
      INDEX2 = 45
      INDEX3 = 45
C
CC     READS TITLE AND DATA CARDS
C
      READ(5,900) TITLE
  900 FORMAT(13A6,A2)
      WRITE(6,901) TITLE
  901 FORMAT(1H,13A6,A2)
      READ(5,9000) NOCL,SALAF,LAMID,NOCOL,COLMAX,SVP,NOVAR
 9000 FORMAT(7I5)
      IF (NOCL .EQ. 0) NOCL = 10
      LAMID = LAMID + 1
      LAMDA(1) = 0.7107
      LAMDA(2) = 1.5418
      LAMDA(3) = 1.79
      IF (NOCOL .EQ. 0) NOCOL = 11
      IF (COLMAX .EQ. 0) COLMAX = 236
      INDMIN = 100
      DO 752 PARAM = 1,3
      DO 751 VAL=1,2000
      OCC(VAL,PARAM) = 0
  751 CONTINUE
  752 CONTINUE
      CALL SETUP(N,MIN,MAX,DATA,IHKL)
      NJ=N
      TOTNO = NJ
      N=N+1
C
CCC    READS NJ RECORDS FROM DISK
CCCCC
CCCCC  AN ILS FILE HAS 99 ON THE NJ+1TH RECORD
CCC    AN IED FILE HAS 999 ON THE NJ+1TH RECORD
C
   80 IF (IHKL(1,N) .EQ. 999) GO TO 7100
      IF (IHKL(1,N) .EQ.  99) GO TO 7222
      GO TO 7224
 7222 IED = 1
      GO TO 7001
 7224 CONTINUE
      GO TO 7101
 7100 CONTINUE
C
CC     READS NJ+1TH RECORD FOR SCALE FACTORS AND OTHER PARAMETERS
C
      IF (NOVAR .EQ. 0 ) NOVAR = IHKL(4,N)
      NUMSCA = IHKL(5,N)
```

```
      IF (NUMSCA .GT. 6) GO TO 862
      IF (NUMSCA .EQ. 0) GO TO 862
      DO 861 NMNN = 1,NUMSCA
      SCALE(NMNN) = DATA(NMNN,N)
  861 CONTINUE
      GO TO 7001
  862 CONTINUE
C
CC     IF NO SCALE FACTORS SETS ALL SCALE FACTORS TO ONE
C
      DO 863 NNNM = 1,TOTNO
      SCALE(IHKL(4,NNNM)) = 1
  863 CONTINUE
 7101 CONTINUE
 7001 CONTINUE
      IF (IED .EQ. 1) WRITE(6,960)
  960 FORMAT(/,1H,' THE DATA COMES FROM AN ILS FILE')
      IF (IED .EQ. 0) WRITE(6,961)
  961 FORMAT(/,1H,' THE DATA COMES FROM AN IED FILE')
      IF (SALAF .EQ. 1) WRITE(6,980)
  980 FORMAT(1H,' AND HAS BEEN SORTED, LISTED AND REFILED.')
      IF (SALAF .EQ. 0) WRITE(6,981)
  981 FORMAT(1H,' AND HAS BEEN SORTED AND LISTED')
      WRITE(6,334) NJ
  334 FORMAT(1H,' THE NUMBER OF REFLECTIONS SORTED AND LISTED IS',I5)
C
CC     THE RANGE OF INDICES IS PRINTED OUT
C
      WRITE(6,333)
  333 FORMAT(//,1X,'  INDEX    RANGE')
      WRITE(6, 78) MIN(1),MAX(1)
      WRITE(6,178) MIN(2),MAX(2)
      WRITE(6,278) MIN(3),MAX(3)
   78 FORMAT(/,1X,'  H   ',2I5)
  178 FORMAT(1X,'  K   ',2I5)
  278 FORMAT(1X,'  L   ',2I5)
      A = SVP
      DO 7010 I = 1,3
      DIFF(I) = MAX(I) -MIN(I)
      IF (DIFF(I) .LT. INDMIN) INDMIN = DIFF(I)
      IF (DIFF(I) .GE. INDMAX) INDMAX = DIFF(I)
 7010 CONTINUE
      DO 6105 I = 1,3
      IF (DIFF(I) .EQ. INDMIN) JAB = I
      IF (DIFF(I) .EQ. INDMAX) JAD = I
      IF (DIFF(I) .NE. INDMIN .AND. DIFF(I) .NE. INDMAX) JAC = I
 6105 CONTINUE
      IF (JAB .EQ. 1) WRITE(6,9521)
 9521 FORMAT(1H, ' THE SLOWEST VARYING INDEX IS H')
      IF (JAB .EQ. 2) WRITE(6,9522)
 9522 FORMAT(1H, ' THE SLOWEST VARYING INDEX IS K')
      IF (JAB .EQ. 3) WRITE(6,9523)
 9523 FORMAT(1H, ' THE SLOWEST VARYING INDEX IS L')
      IF (A .EQ. 0) A = JAB
      SNP = A
      IF(A .EQ. 1) GO TO 6211
      IF(A .EQ. 2) GO TO 6212
      IF(A .EQ. 3) GO TO 6213
 6211 B = 2
      C = 3
        WRITE(6,9533)
 9533 FORMAT (1H, ' THE DATA HAS BEEN SORTED ON INDEX H')
      GO TO 6204
 6212 B = 3
      C = 1
        WRITE(6,9532)
 9532 FORMAT (1H, ' THE DATA HAS BEEN SORTED ON INDEX K')
      GO TO 6204
```

```
 6213 B = 1
      C = 2
        WRITE(6,9531)
 9531 FORMAT (1H, ' THE DATA HAS BEEN SORTED ON INDEX L')
 6204 CONTINUE
      VALM = 0
      NUMVAL = -1
 2200 CONTINUE
      NUMVAL = NUMVAL +1
      DO 7008 N = 1,NJ
      VAL = DATA(1,N)*10.0**NUMVAL  + 0.5
      IF (VAL.GT. VALM) VALM = VAL
 7008 CONTINUE
      WRITE(6,20004) NUMVAL ,NJ,VALM
20004 FORMAT(1X,'NUMVAL NJ VALM',3I6)
      IF (VALM .LT. 100) GO TO 2200
      IF (IED .EQ. 1) GO TO 527
      DO 7004 N = 1,NJ
      DO 389 PARAM = 1,2
C
C      FOR SORTING ON SIN-THETA/LAMDA THE VALUES OF IT ARE MULTIPLIED BY
C     1000 AND THE OCCURRENCE OF EACH SUCH VALUE IS ASCERTAINED. THE
C     TOTAL NUMBER OF REFLECTIONS I DIVIDED BY THE NUMBER OF CLASSES-1
C     AND THE INTEGERS FOR SIN-THETA OVER LAMDA ARE RUN THROUGH UNTIL
C     THE SUM OF THE OCCURRENCES EXCEEDS THE NUMBER OF REFLECTIONS IN A
C     CLASS.
C
      IF (PARAM .EQ.1) VAL = DATA(4,N)*1000.0 + 0.5
C
C      THE INTEGER VAL CAN BE SCALED UP BY A FACTOR OF 10 TO THE POWER
C      OF NUMVAL IF FOBS IS LESS THAN 100.
C
      IF (PARAM .EQ.2) VAL = DATA(1,N)*10.0**NUMVAL + 0.5
      IF(VAL.GT.1999) WRITE(6,20005)VAL,PARAM,NUMVAL
20005 FORMAT(1X,'VAL,PARAM NUMVAL',3I6)
      OCC(VAL,PARAM) = OCC(VAL,PARAM) + 1
  389 CONTINUE
C      L IS THE SLOWEST VARYING INDEX AND ALL INDICES ARE MADE GREATER
C      THAN ZERO BY ADDING (1-MIN(INDEX)).
C
 7004 CONTINUE
      WRITE(6,20006) NJ,TOTNO
20006 FORMAT(1X,'NJ TOTNO',2I6)
C
C      NUM = NO. IN A CLASS
C
      NUM = TOTNO/(NOCL-1)
      DO 383 MM = 1,20
      NSUM(MM) = 0
  383 CONTINUE
      DO 357 PARAM = 1,2
      MM=1
C
C      DATA IS DIVIDED UP INTO CLASSES
C
      NSUM(2)=NSUM(2)+OCC(2000,1)
      LSUM=NSUM(2)
      NUM=(TOTNO-LSUM)/NOCL
      DO 354 VAL=1,2000
      NSUM(PARAM) = NSUM(PARAM) + OCC(VAL,PARAM)
      IF(PARAM.EQ.2) WRITE(6,20010) NSUM(2),(OCC(VAL,IM),IM=1,3)
20010 FORMAT(1X,'NSUM OCC' 4I6)
      IF(NSUM(PARAM).GE.MM*NUM+LSUM) GO TO 353
      IF(NSUM(PARAM) .EQ. TOTNO) GO TO 353
      GO TO 354
  353 LIMIT(PARAM,MM) = VAL
      WRITE(6,20003) NSUM(PARAM),LIMIT(PARAM,MM),MM,VAL
20003 FORMAT(1X,'NSUM LIMIT MM VAL',4I5)
```

```
C
CC       NUMPLN IS THE NUMBER OF PLANES COUNTED
C
      NUMPLN(PARAM,MM) = NSUM(PARAM)
      IF (MM .GT. 1) GO TO 777
C
CC       NONCLS IS NO. OF REFLECTIONS IN CLASS MM.
C
      NONCLS(PARAM,1) = NUMPLN(PARAM,MM)
      GO TO 778
  777 NONCLS(PARAM,MM) = NUMPLN(PARAM,MM) - NUMPLN(PARAM,MM-1)
  778 CONTINUE
      IF(NSUM(PARAM) .EQ. TOTNO) GO TO 4357
      MM = MM + 1
  354 CONTINUE
 4357 MMM(PARAM) = MM
  357 CONTINUE
      WRITE(6,20000) MM
20000 FORMAT(1X,'MM',I5)
      MMM(3) = 6
      DO 358 PARAM = 1,3
      DO 5357 MM = 1,30
      IF (PARAM .EQ. 3) NONCLS(PARAM,MM) = 0
      JSUM(MM) = 0
      FSUM(MM) = 0
      FCSQSM(MM) = 0
      FSQSUM(MM) = 0
 5357 CONTINUE
C
CC       BEGINNING OF STATISTICS CALCULATION.
C
      WRITE(6,20001) MMM(PARAM)
20001 FORMAT(1X,'MMM',I5)
      DO 350 N = 1,TOTNO
      IF ( PARAM .EQ. 1) DATAA(N) = DATA(4,N)*1000.0 +0.5
      IF (PARAM .EQ. 2) DATAA(N) = DATA(1,N)*10**NUMVAL + 0.5
      IF ( PARAM .EQ. 3) DATAA(N) = DATA(1,N)**2 +0.5
      JMM = MMM(PARAM)
      DO 359 MM = 1,JMM
      IF (PARAM .EQ.3) LIMIT(3,MM) = (MM)*DATA(1,N)*2.0*(DATA(2,N))+0.5
      IF(PARAM .EQ. 3 .AND. MM .EQ.6) GO TO 3333
C
CC       GOES THROUGH ALL REFLECTIONS TESTING TO WEE IF THEY LIE BETWEE N
CC      CLASS LIMITS.
C
      IF (DATAA(N) .GT. LIMIT(PARAM,MM)) GO TO 359
      IF (MM .EQ. 1) GO TO 352
 3333 IF (DATAA(N) .LE. LIMIT(PARAM,MM-1)) GO TO 359
C
CC       FOR THE SIGMA STSTISTICS THE NO, IN EACH CLASS IS COUNTED HERE.
C
  352 IF (PARAM .EQ. 3) NONCLS(3,MM) = NONCLS(3,MM) + 1
C
CC       SUMS FOR STATS. ARE ACCUMULATED.
C
      JSUM(MM) = JSUM(MM) + DATA(1,N)
      FSUM(MM) = FSUM(MM) + (ABS(DATA(1,N)- DATA(3,N)))
      FCSQSM(MM) = FCSQSM(MM)+((ABS(DATA(1,N)-DATA(3,N)))/DATA(2,N))**2
      FSQSUM(MM) = FSQSUM(MM) + (DATA(1,N)/DATA(2,N))**2
  359 CONTINUE
  350 CONTINUE
      IF (PARAM .EQ. 2) GO TO 766
      GO TO 767
  766 CONTINUE
      DO 4129 MM = 1,JMM
      LIMIT(2,MM) = LIMIT(2,MM)/(10**NUMVAL)
      WRITE(6,20002) LIMIT(2,MM),MM
20002 FORMAT(1X,'LIMIT MM',2I5)
```

```
 4129 CONTINUE
  767 CONTINUE
C
CC       TABLE TITLES ARE WRITTEN OUT.
C
      IF (PARAM .EQ. 2) WRITE(6,610)
  610 FORMAT(///,1X,'WEIGHTING ANALYSIS IN RANGES BASED ON MAGNITUDES OF
     * STRUCTURE FACTORS')
      IF (PARAM .EQ. 1) WRITE(6,611)
  611 FORMAT(/,1X,'WEIGHTING ANALYSIS WITH RESPECT TO SINE THETA OVER LA
     *MBDA FOR ALL FOBS')
      IF (PARAM .EQ. 3) WRITE(6,612)
  612 FORMAT(///,1X,'WEIGHTING ANALYSIS IN RANGES BASED ON SIGMAS')
      WRITE(6,378)
  378 FORMAT(/,1X,'     RANGE        WDELSQ     RW            R    MNFOBS
     *     ERROR  NO. OF REFLECTIONS')
C
CC       OVERALL SUMS INITIALISED TO ZERO.
C
      ORSUM1 = 0
      ORSUM2 = 0
      ORWSM1 = 0
      ORWSM2 = 0
C
CC       STATS. CALC'D FROM SUMS A CLASS AT A TIME
C
      IF(LSUM.GT.0) JMM=JMM+1
      DO 355 MM = 1,JMM
      IF (NONCLS(PARAM,MM) .EQ. 0) GO TO 355
      WDELSQ = FCSQSM(MM)/NONCLS(PARAM,MM)
      RW = SQRT(FCSQSM(MM)/FSQSUM(MM))
      R = FSUM(MM)/JSUM(MM)
      MNFOBS = JSUM(MM)/NONCLS(PARAM,MM)
      ERROR(MM) =SQRT(FCSQSM(MM)*TOTNO/((TOTNO-NOVAR)*NONCLS(PARAM,MM)))
      IF(PARAM .EQ.3) GO TO 335
      IF (MM .EQ. 1) WRITE(6,367)  LIMIT(PARAM,1),WDELSQ,RW,R,MNFOBS,ERR
     *OR(MM),NONCLS(PARAM,1)
  367 FORMAT(/,1X,'  0    -    ',I3,5F10.3,7X,I3)
      IF (MM.GT. 1) WRITE(6,368) LIMIT(PARAM,MM-1) + 1,LIMIT(PARAM,MM
     *),WDELSQ,RW,R,MNFOBS,ERROR(MM),NONCLS(PARAM,MM)
  368 FORMAT(1X,I3,3X,'-',3X,I3,5F10.3,7X,I3)
      GO TO 337
  335 CONTINUE
      IF (MM .LT. 6)WRITE(6,372) MM-1,MM,WDELSQ,RW,R,MNFOBS,ERROR(MM),NO
     *NCLS(PARAM,MM)
  372 FORMAT(/,1X,I3,'SIGMA-',I1,'SIGMA  'F6.3,4F10.3,6X,I4)
      IF (MM .EQ. 6) WRITE(6,373) MM-1,  WDELSQ,RW,R,MNFOBS,ERROR(MM),NO
     *NCLS(PARAM,MM)
  373 FORMAT(/,1X,I3,'SIGMA- ',7X,         F6.3,4F10.3,6X,I4)
  337 CONTINUE
C
CC       OVERALL SUMS ACCUMULATED.
C
      ORSUM1 = ORSUM1 + FSUM(MM)
      ORSUM2 = ORSUM2 + JSUM(MM)
      ORWSM1 = ORWSM1 + FCSQSM(MM)
      ORWSM2 = ORWSM2 + FSQSUM(MM)
  355 CONTINUE
C
CC       OVERALL STATS. CALC'D.
C
      OR = ORSUM1/ORSUM2
      ORW = SQRT(ORWSM1/ORWSM2)
      OWDELS = ORWSM1/TOTNO
      OMNFOB = ORSUM2/TOTNO
      OERROR = SQRT(ORWSM1/(TOTNO-NOVAR))
      JCAT=1
      IF(LIMIT(2,1).EQ.0)JCAT=2
```

```
      WRITE(6,379) OWDELS,ORW,OR,OMNFOB,OERROR,TOTNO
  379 FORMAT(/,1X,'     OVERALL    ',5F10.3,6X,I4)
      IF (PARAM .EQ. 2) GO TO 7979
      GO TO 9797
 7979 FACTOR=ERROR(JMM-1)/ERROR(JCAT)
      WRITE(6,458) FACTOR
  458 FORMAT(/,1X,'THE FACTOR TO MULTIPLY P BY TO OBTAIN A NEW VALUE FOR
     * IT IS ',F5.3,' AND IT IS THE QUOTIENT OF THE LAST')
      WRITE(6,459)
  459 FORMAT(1X,'FULL ENTRY AND THE FIRST ENTRY IN THE ERROR TABLE')
 9797 CONTINUE
  358 CONTINUE
      CNFSUM = 0
      CNJSUM = 0
      WCNSUM = 0
      WCNQSM = 0
C
CC     CONVENTIONAL R FACTORS USING SCALED FOBS CALC'D
C
      NUMB = 0
      DO 3157 N = 1,TOTNO
      IF (IHKL(4,N) .LE. 0 .OR. IHKL(4,N) .GT. 6) GO TO 288
      GO TO 287
  288 CONTINUE
      IHKL(4,N) = 1
      NUMB = NUMB + 1
      IF (NUMB .GE. 2) GO TO 287
      WRITE(6,285)
  285 FORMAT(1X,72('*'))
      WRITE(6,286)
  286 FORMAT(1X,' THE SCALE FACTOR IDENTIFIER LIES OUTSIDE THE RANGE'/
     *1X,'1-6 FOR AT LEAST ONE OF THE REFLECTIONS AND HAS BEEN SET' /
     *1X,'TO 1 IN SUCH CASES')
      WRITE(6,284)
  284 FORMAT(1X,72('*'))
  287 CONTINUE
      CNFSUM = CNFSUM + DATA(1,N)*SCALE(IHKL(4,N))
      CNJSUM = CNJSUM + (ABS(DATA(1,N)-DATA(3,N)))*SCALE(IHKL(4,N))
      WCNQSM =  WCNQSM + ((ABS(DATA(1,N)-DATA(3,N)))*SCALE(IHKL(4,N))**2
     */DATA(2,N))**2
      WCNSUM = WCNSUM + (DATA(1,N)*SCALE(IHKL(4,N))**2/DATA(2,N))**2
 3157 CONTINUE
      CONVNR = CNJSUM/CNFSUM
      WRITE(6,3158) CONVNR
 3158 FORMAT(///,1X,'CONVENTIONAL R FACTOR = ',F6.3)
      WGTDCR = SQRT(WCNQSM/WCNSUM)
      WRITE(6,3159) WGTDCR
 3159 FORMAT(/,1X,'WEIGHTED R FACTOR = ',F6.3)
C
CC     FOR ANALYSIS ON MILLER INDICES THE MAX. VALUE OF INDICES IS
CC     ALTERED AS IS THE ORDER IN WHICH THEY ARE RUN THROUGH
CC     IN THE NESTED LOOPS.
C
      WRITE(6,614)
  614 FORMAT(/,1X,'WEIGHTING ANALYSIS FOR GIVEN VALUES OF MILLER INDICES
     *')
      GO TO 10000
      DO 526 Z = 1,3
      DO 615 L = 1,INDEX3
      COUNT(L) = 0
      HKLSUM(L) = 0
      HKFSUM(L) = 0
      HKSQSM(L) = 0
      HKQSUM(L) = 0
  615 CONTINUE
      IF (Z .EQ. 1) GO TO 605
      IF (Z .EQ. 2) GO TO 606
      IF (Z .EQ. 3) GO TO 607
```

```
  605 CONTINUE
      ZA = A
      ZB = B
      ZC = C
      GO TO 608
  606 CONTINUE
      ZA = B
      ZB = C
      ZC = A
      GO TO 608
  607 CONTINUE
      ZA = C
      ZB = A
      ZC = B
  608 CONTINUE
      IF(ZA .EQ. 1) WRITE(6,781)
      IF(ZA .EQ. 2) WRITE(6,782)
      IF(ZA .EQ. 3) WRITE(6,783)
  781 FORMAT(/,1X,'H=      WDELSQ      RW        R      MNFOBS     ERROR
     *  NO. OF REFLECTIONS')
  782 FORMAT(/,1X,'K=      WDELSQ      RW        R      MNFOBS     ERROR
     *  NO. OF REFLECTIONS')
  783 FORMAT(/,1X,'L=      WDELSQ      RW        R      MNFOBS     ERROR
     *  NO. OF REFLECTIONS')
      WRITE(6,784)
  784 FORMAT(1X,'    ')
      DO 521 L = 1,MAX(ZA)-MIN(ZA) + 1
      DO 522 M = 1,MAX(ZB)-MIN(ZB) + 1
      DO 523 LL= 1,MAX(ZC)-MIN(ZC) + 1
      IF (ZA .EQ. A) GO TO 601
      IF (ZA .EQ. B) GO TO 602
      IF (ZA .EQ. C) GO TO 603
  601 CONTINUE
      LZ = L
      MZ = M
      LLZ = LL
      GO TO 604
  602 CONTINUE
      LZ = LL
      MZ = L
      LLZ = M
      GO TO 604
  603 CONTINUE
      LZ = M
      MZ = LL
      LLZ = L
  604 CONTINUE
C
CC     UNRECORDED LABEL VALUES ARE SKIPPED BY.
C
      IF (LABEL(LZ,MZ,LLZ) .EQ. 0) GO TO 523
      COUNT(L) = COUNT(L) + 1
C
CC     SUMS ARE ACCUMULARED
C
      HKLSUM(L)   = HKLSUM(L)   +  DATA(1,LABEL(LZ,MZ,LLZ))
      HKFSUM(L)   = HKFSUM(L)   + (ABS( DATA(1,LABEL(LZ,MZ,LLZ))- DATA(3,L
     *ABEL(LZ,MZ,LLZ))))
      HKSQSM(L)   =  HKSQSM(L)   + ((ABS( DATA(1,LABEL(LZ,MZ,LLZ))- DATA(3
     *,LABEL(LZ,MZ,LLZ))))/ DATA(2,LABEL(LZ,MZ,LLZ)))**2
      HKQSUM(L)   = HKQSUM(L)   + ( DATA(1,LABEL(LZ,MZ,LLZ))/ DATA(2,LABEL
     *(LZ,MZ,LLZ)))**2
  523 CONTINUE
  522 CONTINUE
  521 CONTINUE
      ERRSUM = 0
      DO 524 L = 1,(MAX(ZA)-MIN(ZA) +1)
      IF(HKLSUM(L) .EQ. 0) GO TO 524
```

```
      IF (HKQSUM(L) .EQ. 0) GO TO 524
C
CC     STATS. ARE CALC'D AND WRITTEN OUT A CLASS AT A TIME.
C
      WDELSQ = HKSQSM(L)/COUNT(L)
      ERRSUM = ERRSUM + HKSQSM(L)
      RW = SQRT(HKSQSM(L)/HKQSUM(L))
      R  = HKFSUM(L)/HKLSUM(L)
      MNFOBS = HKLSUM(L)/COUNT(L)
      ERROR(L) = SQRT(HKSQSM(L)*TOTNO/((TOTNO-NOVAR)*COUNT(L)))
      ACTL = L + (MIN(ZA)-1)
      WRITE(6,525) ACTL,WDELSQ,RW,R,MNFOBS,ERROR(L),COUNT(L)
  525 FORMAT(1H,I3,5F10.3,6X,I4)
  524 CONTINUE
  526 CONTINUE
      OERROR = SQRT(ERRSUM/(TOTNO-NOVAR))
C
CC     'BAD' REFLECTIONS TESTED FOR AND WRITTEN OUT.
C
      WRITE(6,532)
  532 FORMAT(///,1X,'LIST OF REFLECTIONS WHERE FOBS-FCALC DIVIDED BY ERR
     *OR IN OBSERVATION OF UNIT WEIGHT IS GREATER THAN  3, FOR REFINEMEN
     *T ON FOBS')
      WRITE(6,533)
  533 FORMAT(/,1X,'     H     K     L       FOBS      FCALC     SINTHL TWO THE
     *TA         NREF   NSIG ON F')
  527 CONTINUE
      DO 6109 L = 1,(MAX(A) - MIN(A) +1)
      DO 6110 M = 1,(MAX(B)-MIN(B) + 1)
      DO 6111 LL = 1,(MAX(C) -MIN(C) + 1)
      IF (LABEL(L,M,LL) .EQ. 0) GO TO 6111
      IF (IED .EQ. 1) GO TO 531
      IF(ABS((DATA(1,LABEL(L,M,LL))-DATA(3,LABEL(L,M,LL)))/DATA(2,LABEL(
     *L,M,LL))).GE.3*OERROR) GO TO 530
      GO TO 531
  530 CONTINUE
      WRITE(6,636) IHKL(1,LABEL(L,M,LL)),IHKL(2,LABEL(L,M,LL)),IHKL(3,LA
     *BEL(L,M,LL)),DATA(1,LABEL
     *(L,M,LL)), DATA(3,LABEL(L,M,LL)), DATA(4,LABEL(L,M,LL)),
     *360.0*ARSIN( DATA(4,LABEL(L,M,LL))*LAMDA(LAMID))/3.14159       ,IHKL
     *(5,LABEL(L,M,LL)), ABS(DATA(1,LABEL(L,M,LL))-DATA(3,LABEL(L,M,LL))
     *)/(OERROR*DATA(2,LABEL(L,M,LL)))
  636 FORMAT(1X,3I5,6F10.2)
  531 CONTINUE
      IF (SALAF .EQ. 1) GO TO 4951
      GO TO 4952
 4951 CONTINUE
      WRITE(STDT,END=90) (DATA(JKJ,LABEL(L,M,LL)),JKJ = 1,6),(IHKL(IKI,L
     *ABEL(L,M,LL)),IKI = 1,5)
   90 CONTINUE
 4952 CONTINUE
 6111 CONTINUE
 6110 CONTINUE
 6109 CONTINUE
C
CC     NONCOL IS THE NUMBER IN A COLUMN.
C
      NONCOL = ((TOTNO+4.0*(DIFF(SNP)+1))/NOCOL + 0.9999)
      GO TO 45
C
CC     RETURNS TO HERE IF AN INDEX TITLE COMES AT THE BOTTOM OF A COLUMN
C
 5000 CONTINUE
      DO 4781 JY=1,1300
      DO 4782 JW = 1,12
      DO 4783 JX = 1,4
      PUBDAT(JX,JW,JY) = 0.0
 4783 CONTINUE
```

```
 4782 CONTINUE
 4781 CONTINUE
      IF (NONCOL .LT. COLMAX) GO TO 44
      COLMAX = COLMAX + 2
      GO TO 45
   44 NONCOL = NONCOL + 2
   45 CONTINUE
      ANONCO = NONCOL
      NNPAGE = (ANONCO/COLMAX + 0.9999)
      LO = 1
      MO = 1
      LLO = 1
      DO 3002 JD = 1,NNPAGE
      NOCOLL = NOCOL
      PUBDAT(2,1,1) = -1000.0
      PUBDAT(2,1,2) = -1000.0
      PUBDAT(2,1,3) = -1000.0
      PUBDAT(2,1,4) = -1000.0
      PUBDAT(1,1,3) = MIN(A)
      J = 5
      IF(NONCOL .LE. COLMAX) GO TO 400
      JCA = COLMAX*(JD-1) + 1
      IF (JD .LT. NNPAGE) JDA = COLMAX*JD
      IF (JD .EQ. NNPAGE) JDA = NONCOL
      GO TO 500
  400 JCA = 1
C
CC       DETERMINATION OF COLUMNS.
C
      JDA = NONCOL
  500 CONTINUE
C
CC       PLACES DATA IN PUBDAT THE ARRAY PRINTED OUT WITH NOCOL COLUMNS.
C
      I = 1
      IF (JD .GT. 1) J = JCA
      DO 4901 L = LO,DIFF(A) + 1
      DO 4902 M = MO,DIFF(B) + 1
      MO = 1
      DO 4903 LL = LLO,DIFF(C) + 1
      LLO = 1
      IF (LABEL(L,M,LL) .EQ. 0) GO TO 4950
      PUBDAT(1,I,J) = M + MIN(B) -1
      PUBDAT(2,I,J) = LL+ MIN(C) -1
      PUBDAT(3,I,J) = DATA(1,LABEL(L,M,LL))
      PUBDAT(4,I,J) = DATA(3,LABEL(L,M,LL))
      J = J + 1
      JS = JDA -J
      IF (JS .LE. -1) GO TO 4904
      GO TO 4906
 4904 CONTINUE
      J = JCA
      I = I + 1
      JI = NOCOL-I
      IF (JI .EQ. -1) GO TO 4911
      GO TO 4912
 4911 CONTINUE
      LO = L
      MO = M
      LLO = LL+1
      GO TO 4900
 4912    CONTINUE
 4906 CONTINUE
 4950 CONTINUE
 4903 CONTINUE
 4902 CONTINUE
      IF (L+MIN(A) .GT. MAX(A)) GO TO 4914
      PUBDAT(2,I,J+1) = -1000.0
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      PUBDAT(2,I,J+2) = -1000.0
      PUBDAT(2,I,J+3) = -1000.0
      PUBDAT(2,I,J  ) = -1000.0
      PUBDAT(1,I,J+2) = L+MIN(A)
 4914 CONTINUE
      J = J + 4
 4901 CONTINUE
 4900 CONTINUE
      DO 4998 I = 1,NOCOL
      IF (PUBDAT(2,I,JDA-1) .EQ. -1000) GO TO 5000
      IF (PUBDAT(2,I,JDA) .EQ. -1000) GO TO 5000
 4998 CONTINUE
 3002 CONTINUE
      NPAGE = NNPAGE
C
C       WRITES ROW-COLUMN INFORMATION.
C
      WRITE(6,9502)
 9502 FORMAT(///,1H, ' THE NUMBER OF ROWS IS')
      WRITE(6,9512) NONCOL
 9512 FORMAT('+',24X, I3)
      WRITE(6,9501)
 9501 FORMAT(1H,' THE NUMBER OF COLUMNS IS')
      WRITE(6,9511) NOCOL
 9511 FORMAT('+',27X,I2)
      DO 3001 JA = 1,NPAGE
      IF (NONCOL .LE. COLMAX) GO TO 600
      JC = COLMAX*(JA-1) + 1
      IF (JA .EQ. NPAGE) JD = NONCOL
      IF (JA .LT. NPAGE) JD = COLMAX*JA
      GO TO 700
  600 JC = 1
      JD = NONCOL
  700 CONTINUE
      DO 3003 U = 1,NOCOL,6
      JT1 = 0
      JT2 = 0
      JT3 = 0
      JT4 = 0
      JT5 = 0
      JT6 = 0
C
C       WRITES DATA PAGE TITLE AND ALIGNMENT SYMBOLS.
C
      WRITE(6,1200)
 1200 FORMAT(////,1X,6('.ALIGNMENT.',9X),'.ALIGNMENT.')
      WRITE(6,1201)
 1201 FORMAT('1'///,1X,6('.ALIGNMENT.',9X),'.ALIGNMENT.')
      WRITE(6,1202)
 1202 FORMAT(////////,1X,'    ')
      IF (IED .EQ.1) GO TO 5060
      IF(SNP .EQ. 1) WRITE (6,4001)
 4001 FORMAT(//,1X,3X,6(' K    L  OBS CALC     '))
      IF(SNP .EQ. 2) WRITE (6,4002)
 4002 FORMAT(//,1X,3X,6(' H    L  OBS CALC     '))
      IF(SNP .EQ. 3) WRITE (6,4003)
 4003 FORMAT(//,1X,3X,6(' H    K  OBS CALC     '))
      GO TO 6000
 5060 IF (SNP .EQ. 1) WRITE(6,5001)
 5001 FORMAT(//,1X,3X,6(' K    L IOBS IRAW     '))
      IF (SNP .EQ. 2) WRITE(6,5011)
 5011 FORMAT(//,1X,3X,6(' H    L IOBS IRAW     '))
      IF (SNP .EQ. 3) WRITE(6,5021)
 5021 FORMAT(//,1X,3X,6(' H    K IOBS IRAW     '))
 6000 CONTINUE
      WRITE(6,888)
  888 FORMAT(1X, '   ')
C
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C       FOR EACH OF THE SIX COLUMNS PER PAGE WRITES OUT PUBDAT.
C
        V = U+1
        W = U+2
        X = U+3
        Y = U+4
        Z = U+5
C
CC        ADDS FURTHER SETS OF COLUMNS UNTIL NOCOL IS REACHED.
CC        IF NONCOL GREATER THAN 240 BEGINS A NEW PAGE.
CC        THE JTN COUNTERS ARE USED TO OBTAIN BLANKS AND TITLE WHEN THE
CC      SORTING INDEX CHANGES.
C
        DO 3000 J = JC,JD
        IF (PUBDAT(2,U,J) .EQ. -1000.0) GO TO 1100
        WRITE (C1,1000)(PUBDAT(PNPP,U,J),PNPP = 1,4)
 1000   FORMAT(I3,1X,I3,1X,I4,1X,I4)
        GO TO 2000
 1100   JT1 = JT1 + 1
        IF (JT1.EQ. 3) GO TO 1110
        WRITE(C1,1151)
 1151   FORMAT(1X '    ')
        IF (JT1 .EQ. 4) JT1 = 0
        GO TO 2000
 1110   IF (SNP .EQ. 1) WRITE(C1,2008) PUBDAT(1,U,J)
 2008   FORMAT('  **** H =',I2,' ****')
        IF (SNP .EQ. 2) WRITE(C1,2009) PUBDAT(1,U,J)
 2009   FORMAT('  **** K =',I2,' ****')
        IF (SNP .EQ. 3) WRITE(C1,2010) PUBDAT(1,U,J)
 2010   FORMAT('  **** L =',I2,' ****')
 2000   CONTINUE
        IF (PUBDAT(2,V,J) .EQ. -1000.0) GO TO 1101
        WRITE (C2,1001)(PUBDAT(PNPP,V,J),PNPP = 1,4)
 1001   FORMAT(I3,1X,I3,1X,I4,1X,I4)
        GO TO 2001
 1101   JT2 = JT2 + 1
        IF (JT2 .EQ. 3) GO TO 1111
        WRITE(C2,1152)
 1152   FORMAT(1X '    ')
        IF (JT2 .EQ. 4) JT2 = 0
        GO TO 2001
 1111   IF (SNP .EQ. 1) WRITE(C2,2011) PUBDAT(1,V,J)
 2011   FORMAT('  **** H =',I2,' ****')
        IF (SNP .EQ. 2) WRITE(C2,2012) PUBDAT(1,V,J)
 2012   FORMAT('  **** K =',I2,' ****')
        IF (SNP .EQ. 3) WRITE(C2,2013) PUBDAT(1,V,J)
 2013   FORMAT('  **** L =',I2,' ****')
 2001   CONTINUE
        IF (PUBDAT(2,W,J) .EQ. -1000.0) GO TO 1102
        WRITE (C3,1002)(PUBDAT(PNPP,W,J),PNPP = 1,4)
 1002   FORMAT(I3,1X,I3,1X,I4,1X,I4)
        GO TO 2002
 1102   JT3 = JT3 + 1
        IF (JT3 .EQ. 3) GO TO 1112
        WRITE(C3,1153)
 1153   FORMAT(1X '    ')
        IF (JT3 .EQ. 4) JT3 = 0
        GO TO 2002
 1112   IF (SNP .EQ. 1) WRITE(C3,2014) PUBDAT(1,W,J)
 2014   FORMAT('  **** H =',I2,' ****')
        IF (SNP .EQ. 2) WRITE(C3,2015) PUBDAT(1,W,J)
 2015   FORMAT('  **** K =',I2,' ****')
        IF (SNP .EQ. 3) WRITE(C3,2016) PUBDAT(1,W,J)
 2016   FORMAT('  **** L =',I2,' ****')
 2002   CONTINUE
        IF (PUBDAT(2,X,J) .EQ. -1000.0) GO TO 1103
        WRITE (C4,1003)(PUBDAT(PNPP,X,J),PNPP = 1,4)
 1003   FORMAT(I3,1X,I3,1X,I4,1X,I4)
```

```
      GO TO 2003
 1103 JT4 = JT4 + 1
      IF (JT4 .EQ. 3) GO TO 1113
      WRITE(C4,1154)
 1154 FORMAT(1X '    ')
      IF (JT4 .EQ. 4) JT4 = 0
      GO TO 2003
 1113 IF (SNP .EQ. 1) WRITE(C4,2017) PUBDAT(1,X,J)
 2017 FORMAT('  **** H =',I2,' ****')
      IF (SNP .EQ. 2) WRITE(C4,2018) PUBDAT(1,X,J)
 2018 FORMAT('  **** K =',I2,' ****')
      IF (SNP .EQ. 3) WRITE(C4,2019) PUBDAT(1,X,J)
 2019 FORMAT('  **** L =',I2,' ****')
 2003 CONTINUE
      IF (PUBDAT(2,Y,J) .EQ. -1000.0) GO TO 1104
      WRITE (C5,1004)(PUBDAT(PNPP,Y,J),PNPP = 1,4)
 1004 FORMAT(I3,1X,I3,1X,I4,1X,I4)
      GO TO 2004
 1104 JT5 = JT5 + 1
      IF (JT5 .EQ. 3) GO TO 1114
      WRITE(C5,1155)
 1155 FORMAT(1X '    ')
      IF (JT5 .EQ. 4) JT5 = 0
      GO TO 2004
 1114 IF (SNP .EQ. 1) WRITE(C5,2020) PUBDAT(1,Y,J)
 2020 FORMAT('  **** H =',I2,' ****')
      IF (SNP .EQ. 2) WRITE(C5,2021) PUBDAT(1,Y,J)
 2021 FORMAT('  **** K =',I2,' ****')
      IF (SNP .EQ. 3) WRITE(C5,2022) PUBDAT(1,Y,J)
 2022 FORMAT('  **** L =',I2,' ****')
 2004 CONTINUE
      IF (PUBDAT(2,Z,J) .EQ. -1000.0) GO TO 1105
      WRITE (C6,1005)(PUBDAT(PNPP,Z,J),PNPP = 1,4)
 1005 FORMAT(I3,1X,I3,1X,I4,1X,I4)
      GO TO 2005
 1105 JT6 = JT6 + 1
      IF (JT6 .EQ. 3) GO TO 1115
      WRITE(C6,1156)
 1156 FORMAT(1X '    ')
      IF (JT6 .EQ. 4) JT6 = 0
      GO TO 2005
 1115 IF (SNP .EQ. 1) WRITE(C6,2023) PUBDAT(1,Z,J)
 2023 FORMAT('  **** H =',I2,' ****')
      IF (SNP .EQ. 2) WRITE(C6,2024) PUBDAT(1,Z,J)
 2024 FORMAT('  **** K =',I2,' ****')
      IF (SNP .EQ. 3) WRITE(C6,2025) PUBDAT(1,Z,J)
 2025 FORMAT('  **** L =',I2,' ****')
 2005 CONTINUE
      WRITE (6,999) C1,C2,C3,C4,C5,C6
  999 FORMAT('+'/,3X,3A6,5(2X,3A6))
 3000 CONTINUE
 3003 CONTINUE
 3001 CONTINUE
      WRITE(6,1203)
 1203 FORMAT(////,1X,6('.ALIGNMENT.',9X),'.ALIGNMENT.')
10000 CONTINUE
      STOP
      END
```

```
PROGRAM BONDSTAT
C           ********************
CC          READS TITLE,NUMBER OF BONDS
CC          READS TITLE,NUMBER OF BOND TYPES,MAXIMUM BOND LENGTH,
CC          CELL CONSTANTS,BOND TYPES,ATOM PARAMETERS(2 CARDS EACH)
CCC
CCC         REQUIRES ASYMMETRIC UNIT TO BE A CONNECTED CHEMICAL UNIT
CCC
CCC         WRITES OUT CALCULATED BOND LENGTHS
CCC
CCC         CALCULATES STANDARD DEVIATIONS AND MEANS OF THE SPECIFIED
CCC         TYPES AND PRINTS THEM OUT
CCC         ********************
CCC       INPUT
CCC       *****
CCC       TITLE       13A6,A2
CCC       NUMBER OF BOND TYPES, MAXIMUM BOND LENGTH      I5,F10.6
CCC       CELL CONSTANTS       6F10.6       (ANGLES)
CCC       BOND TYPES       A2,3X,A2       1 PER CARD,NBONDT OF THEM
C         ATOM PARAMETERS          AS FOR CUCLS     2  CARDS PER ATOM
      REAL NAME,NNAME
      DIMENSION TITLE(14)
      DIMENSION TAB1(6),TAB2(6)
      DIMENSION DELTAX(3)
      DIMENSION CELL(6)
      DIMENSION NAME(150,6),NNAME(2,500),X(3,150),SUM(100),DIST(500),BON
     *D(100,2),SUMSQ(100),NUM(100)
C
CC          READS TITLE,NUMBER OF BONDS
CC          READS TITLE,NUMBER OF BOND TYPES,MAXIMUM BOND LENGTH,
CC          NUMBER OF SYMBOLS REQUIRED FROM ATOM LABEL,
CC          CELL CONSTANTS,BOND TYPES,ATOM PARAMETERS(2 CARDS EACH)
C
      LIM=500
      READ(5,10000) TITLE
10000 FORMAT(13A6,A2)
      WRITE(6,10001) TITLE
10001 FORMAT(30X,14A6)
      READ(5,50)NBONDT,NOID,NOID2,D,DMIN
   50 FORMAT(3I5,2F10.6)
      WRITE(6,47) NBONDT,D,NOID,NOID2
   47 FORMAT(1X,'THE NUMBER OF BOND TYPES EXAMINED IS ',I4,' FOR ATOMS
     *LESS THAN ',F5.1,'A APART.  NOID = ',I1,' NOID2 = ',I1)
      DD=D**2
      DDMIN=DMIN**2
      READ(5,51)TAB1
      READ(5,51)TAB2
   51 FORMAT(6I1)
      READ(5,49) CELL
   49 FORMAT(6F10.6)
      WRITE(6,45) CELL
   45 FORMAT(1X,'CELL CONSTANTS ARE ',6F10.6)
      DO 10 K=1,NBONDT
      READ(5,60)BOND(K,1),BOND(K,2)
   60 FORMAT(A6,4X,A6)
   10 CONTINUE
      DO 100 J=1,150
      READ(5,500,END=200)(NAME(J,JJ),JJ=1,6),(X(II,J),II=1,3)
  500 FORMAT(6A1,24X,3F10.6)
      X(3,J)=X(3,J)*CELL(3)+X(1,J)*COS(CELL(5)*ATAN(1.0)/45.0)*CELL(1)
      X(2,J)=X(2,J)*CELL(2)
      X(1,J)=X(1,J)*SIN(CELL(5)*ATAN(1.0)/45.0)*CELL(1)
      READ(5,501) DUMMY
  501 FORMAT(F6.1)
  100 CONTINUE
  200 N=J-1
C
```

```
C           CALCULATES BOND LENGTHS FOR ALL BONDS IN STRUCTURE
CC          REQUIRES ASYMMETRIC UNIT TO BE A CONNECTED CHEMICAL UNIT
C
      DO 2000 JJ=1,N-1
      DO 300 JK=JJ+1,N
      DIST2=0
      DO 400 I=1,3
      DIST2=DIST2+(X(I,JJ)-X(I,JK))**2
      IF(I.LT.3) GO T O 400
      IF(DIST2.GT.DD) GO TO 300
       IF(DIST2.LT.DDMIN) GO TO 300
      NN=NN+1
      IF(NN.GT.LIM) GO TO 600
      DIST(NN)=DIST2
      DO 297 JE=1,2
  297 NNAME(JE,NN)='      '
      DO 298 L=1,NOID
      NNAME(1,NN)=CONCAT(NNAME(1,NN),NAME(JJ,TAB1(L)),(7-L)*8-1,47,8)
  298 CONTINUE
      DO 296 L=1,NOID2
      NNAME(2,NN)=CONCAT(NNAME(2,NN),NAME(JK,TAB2(L)),(7-L)*8-1,47,8)
  296 CONTINUE
      WRITE(6,301)(NAME(JJ,LN),LN=1,6),(NAME(JK,LM),LM=1,6),NN,SQRT(DIST
     *2)
  301 FORMAT(1X,2(6A1,2X),I5,F10.6)
  400 CONTINUE
  300 CONTINUE
 2000 CONTINUE
      GO TO 700
C
CC          WRITES OUT CALCULATED BOND LENGTHS
C
  600 WRITE(6,800)D,JJ,JK
  800 FORMAT(1X,'500 DISTANCES LESS THAN',F5.3,' HAVE BEEN CALCULATED AN
     *D JJ= ',I3,' JK= ',I3)
      NN=NN-1
  700 CONTINUE
C
CC          CALCULATES STANDARD DEVIATIONS AND MEANS OF THE SPECIFIED
CC          TYPES AND PRINTS THEM OUT
C
      DO 900 JR=1,NN
      DO 910 NB=1,NBONDT
      IF(NNAME(1,JR).IS.BOND(NB,1).AND.NNAME(2,JR).IS.BOND(NB,2)) GO TO
     *920
  910 CONTINUE
      GO TO 900
  920 CONTINUE
      SUM(NB)=SUM(NB)+SQRT(DIST(JR))
      SUMSQ(NB)=SUMSQ(NB)+DIST(JR)
      NUM(NB)=NUM(NB)+1
  900 CONTINUE
      DO 980 M=1,NBONDT
      SD=SQRT(( SUMSQ(M)-SUM(M)**2/NUM(M))/(NUM(M)-1) )
      WRITE(6,930) NUM(M),BOND(M,1),BOND(M,2),SD,SUM(M)/NUM(M)
  930 FORMAT(1X,'THE STANDARD DEVIATION OF THE',I4,' BONDS ',A6,'-',A6,'
     *IS',F6.4,'A. THE MEAN BOND LENGTH IS ',F6.4,'A.')
  980 CONTINUE
      STOP
      END
```

```
      SAMPLE INPUT

      BOND LENGTH STATISTICS FOR AS S ZN COMPOUND
    8     4     3  3.0      1.5
1235
125
32.508     18.489     30.589     90.0       95.699     90.0
AS(1       S(1
ZN(1       S(1
AS(2       S(2
ZN(2       S(2
AS(3       S(3
ZN(3       S(3
AS(4       S(4
ZN(4       S(4
```

```
PROGRAM SCALE

FILE   1=BITRI/IN,UNIT=DISK,RECORD=11,BLOCKING=90,SAVE=7,AREA=900*8
FILE   2=BITRI/OUT,UNIT=DISK,RECORD=11,BLOCKING=90,SAVE=7,AREA=900*8
       DIMENSION INPUT(20),PROCEZ(40,20)
       DIMENSION DROCEZ(1,30)
       DIMENSION DAT1(30,80),DAT2(30,80),COUNT1(30,80)
       DIMENSION SCAL1(30,80),SCAL2(30,80)
       INT=1
       SIG=2
       H=7
       K=8
       L=9
       NREF=11
       N=11
       NUM=5040
C
CC      READS REFLECTION DATA FROM FILE
CC      SORTS OUT HK0 AND -HK0 REFLECTIONS
C
  100  CONTINUE
       IVXX=1
       READ(IVXX,END=99)(INPUT(J),J=1,N)
   99  CONTINUE
       IF(ABS(INPUT(NREF)).GT. NUM) GO TO 400
       IF(INPUT(L).NE.0) GO TO 100
       IF(INPUT(H).LT.0) GO TO 200
       IF(INPUT(H).GT.0) GO TO 300
       GO TO 100
  200  CONTINUE
       INPUT(K)=INPUT(K)+1
       DAT1(ABS(INPUT(H)),INPUT(K))=INPUT(INT)
       GO TO 100
  300  CONTINUE
       DATA
       INPUT(K)=INPUT(K)+1
       DAT2(ABS(INPUT(H)),INPUT(K))=INPUT(INT)
       GO TO 100
  400  CONTINUE
       REWIND IVXX
  500  CONTINUE
       READ(IVXX,END=199)(INPUT(J),J=1,N)
  199  CONTINUE
       IVYY=2
       IF(ABS(INPUT(NREF)).GT.7308) GO TO 1500
       IF(ABS(INPUT(NREF)).GT.NUM.AND.ABS(INPUT(NREF)) .LE.7308) GO TO 40
      *00
       IF(ABS(INPUT(NREF)).GT.2303.AND.ABS(INPUT(NREF)).LT.2851) GO TO 40
      *00
       GO TO 4001
 4000  CONTINUE
       WRITE(IVYY)(INPUT(J),J=1,N)
       GO TO 500
 4001  CONTINUE
       INPUT(K)=INPUT(K)+1
       IF(INPUT(L).EQ.0) GO TO 600
C
CC       ESTABLISHES SCALE FACTORS FOR HK0 REFLECTIONS
C
       GO TO 700
  600  CONTINUE
       IF(COUNT.GT.0) GO TO 800
       IF(DAT1(ABS(INPUT(H)),INPUT(K)).LE.0) GO TO 1700
       SCAL1(ABS(INPUT(H)),INPUT(K))=(DAT2(ABS(INPUT(H)),INPUT(K))/DAT1
      *(ABS(INPUT(H)),INPUT(K))+1)*0.5
       GO TO 1800
 1700  CONTINUE
       SCAL1(ABS(INPUT(H)),INPUT(K))=1
```

```
 1800 CONTINUE
      COUNT=0
  700 CONTINUE
      COUNT = COUNT+1
      DO 900 JJJ=1,N
      PROCEZ(COUNT,JJJ)=INPUT(JJJ)
  900 CONTINUE
      GO TO 500
  800 CONTINUE
      IF(DAT1(ABS(INPUT(H)),INPUT(K)).LE.0) GO TO 1900
      SCAL2(ABS(INPUT(H)),INPUT(K))=(DAT2(ABS(INPUT(H)),INPUT(K))/DAT1
     *(ABS(INPUT(H)),INPUT(K))+1)*0.5
      GO TO 2000
 1900 CONTINUE
      SCAL2(ABS(INPUT(H)),INPUT(K))=1
 2000 CONTINUE
      DROCEZ(1,H)=PROCEZ(1,H)
      DROCEZ(1,K)=PROCEZ(1,K)
      IF(SCAL2(ABS(INPUT(H)),INPUT(K)).EQ.0.5) SCAL2(ABS(INPUT(H)),I
     *NPUT(K))=1.0
      IF(SCAL1(ABS(DROCEZ(1,H)),DROCEZ(1,K)).EQ.0.5) SCAL1(ABS(DROCEZ(1,
     *H)),DROCEZ(1,K)) = 1.0
      IF(INPUT(H).GT.0) SCAL2(ABS(INPUT(H)),INPUT(K)) =
     *0.5*(1.0+1.0/(2.0*(SCAL2(ABS(INPUT(H)),INPUT(K))-0.5)))
      IF(DROCEZ(1,H).GT.0) SCAL1(ABS(DROCEZ(1,H)),DROCEZ(1,K)) =
     *0.5*(1.0+1.0/(2.0*(SCAL1(ABS(DROCEZ(1,H)),DROCEZ(1,K))-0.5)))
C
CC       SCALES HKL REFLECTIONS
C
      DO 1000 JJ=1,COUNT
      JJ= JJ-1
      SCALE=((COUNT-JJ)/COUNT)*SCAL1(ABS(DROCEZ(1,H)),DROCEZ(1,K))
     *+JJ*SCAL2(ABS(INPUT(H)),INPUT(K))/COUNT
      JJ= JJ+1
      PROCEZ(JJ,K)=PROCEZ(JJ,K)-1
      PROCEZ(JJ,INT)=PROCEZ(JJ,INT)*SCALE
      PROCEZ(JJ,SIG)=PROCEZ(JJ,SIG)*SCALE
 3000 CONTINUE
      WRITE(6,106)(PROCEZ(JJ,M),M=1,N)
  106 FORMAT(1X,11F12.1)
      WRITE(IVYY)(PROCEZ(JJ,M),M=1,N)
 1000 CONTINUE
      IF(ABS(INPUT(NREF)).EQ.NUM) GO TO 1300
      DO 1100 JK=1,COUNT
      DO 1200 JL=1,N
      PROCEZ(JK,JL)=0
 1200 CONTINUE
 1100 CONTINUE
      COUNT=0
      GO TO 600
 1300 CONTINUE
      PROCEZ(1,INT)=INPUT(INT)*SCAL2(ABS(INPUT(H)),INPUT(K))
      PROCEZ(1,SIG)=INPUT(SIG)*SCAL2(ABS(INPUT(H)),INPUT(K))
      PROCEZ(1,NREF)=5040
      PROCEZ(1,K)=PROCEZ(1,K)+1
C
CC       WRITES SCALED REFLECTION DATA TO PRINTER AND FILE
C
      WRITE(6,106)(PROCEZ(1,MK),MK=1,11)
      WRITE(IVYY)(PROCEZ(1,MN),MN=1,N)
      GO TO 500
 1500 CONTINUE
      PROCEZ(1,H) = 99
      PROCEZ(1,K) = 99
      PROCEZ(1,L) = 99
      WRITE(IVYY)(PROCEZ(1,J),J=1,N)
      LOCK IVYY
      STOP
```